Part I Approximate Hartree-Fock Wavefunctions One-electron Properties and Electronic Structure of the Water Molecule

Part II Perturbation-Variational Calculation of the Nuclear Spin-Spin Isotropic Coupling Constant in HD

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To my father and my mother

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Abstract. Part I.

Several approximate Hartree-Fock SCF wavefunctions for the ground electronic state of the water molecule have been obtained using an increasing number of multicenter s, p, and d Slater-type atomic orbitals as basis sets. The predicted charge distribution has been extensively tested at each stage by calculating the electric dipole moment, molecular quadrupole moment, diamagnetic shielding, Hellmann-Feynman forces, and electric field gradients at both the hydrogen and the oxygen nuclei. It was found that a carefully optimized minimal basis set suffices to describe the electronic charge distribution adequately except in the vicinity of the oxygen nucleus. Our calculations indicate, for example, that the correct prediction of the field gradient at this nucleus requires a more flexible linear combination of p-orbitals centered on this nucleus than that in the minimal basis set. Theoretical values for the molecular octopole moment components are also reported.

Abstract. Part II.

The perturbation-variational theory of R. M. Pitzer for nuclear spin-spin coupling constants is applied to the HD molecule. The zero-order molecular orbital is described in terms of a single 1s Slater-type basis function centered on each nucleus. The first-order molecular orbital is expressed in terms of these two functions plus one singular basis function each of the types $\frac{e^{-r}}{r}$ and $e^{-r} \ln r$ centered on one of the nuclei. The new kinds of molecular integrals were evaluated to high accuracy using numerical and analytical means. The value of the HD spin-spin coupling constant calculated with this near-minimal set of basis functions is $J_{HD} = +96.6$ cps. This represents an improvement over the previous calculated value of +120 cps obtained without using the logarithmic basis function but is still considerably off in magnitude compared with the experimental measurement of $J_{HD} = +43.0 \pm 0.5$ cps.

TABLE OF CONTENTS

Part I: Approximate Hartree-Fock Wavefunctions, One-Electron Properties, and Electronic Structure of the Water Molecule

TABLE OF CONTENTS

Part II: Perturbation-Variational Calculation of the Nuclear Spin-Spin Isotropic Coupling Constant in HD

PART I

APPROXIMATE HARTREE-FOCK WAVEFUNCTIONS ONE-ELECTRON PROPERTIES AND ELECTRONIC STRUCTURE OF THE WATER MOLECULE

1. Introduction

For several decades now the structure of molecules and crystals, meaning the arrangement of nuclear centers therein, have been successfully elucidated by spectroscopic and other means. The determination of electronic density distributions, however, poses to this date a formidable experimental problem. One approach is the extraction of the electronic density function from X-ray diffraction intensities.[1] It appears, however, that the density function can be determined far more accurately through theoretical calculation of the electronic wavefunction than through any experimental means at the present time. This then provides a motivation for the calculation of molecular electronic wavefunctions.

The first part of this thesis is concerned with the calculation of approximate Hartree-Fock wavefunctions and one-electron properties of the water molecule in the ground electronic state. Such a calculation is particularly of interest for the following reasons: (i) water plays a fundamental role in chemistry and biology by virtue of its unusual bulk properties; (ii) from a theoretical point of view, the water molecule is a prototype triatomic molecule since only one of the three atoms involved has inner shells; (iii) an extensive calculation on the water molecule is economically feasible; (iv) finally, experimental values for many of its properties are already known and hence facilitate the evaluation of the calculated charge distribution.

From the above considerations, it is not surprising that ab initio calculation of the electronic structure of the water molecule has received considerable attention. In the following subsection, the most well-known calculations are summarized.

1.1 Previous ab initio calculations on the water molecule

The first ab initio wavefunction calculation that took into account all ten electrons in the water molecule is that of Ellison and Shull[2] who reported an approximate Hartree-Fock wavefunction for the molecule in the ground electronic state in 1955. Ellison and Shull's wavefunction was based on inaccurate values for three-center integrals, however, and hence there would be no valid justification in discussing their results here.

The pioneering calculation on the water molecule appears to be that of Boys et al.[3] who evaluated all necessary integrals accurately. Employing eight Slater-type atomic orbitals as basis functions, they went beyond the Hartree-Fock approximation by including more than one Slater determinant in the wavefunction. The Slater-type basis functions used were not specified and no wavefunctions were tabulated. However, theoretical values for the dipole moment and vibrational force constants were given and compared favourably with experimental values.

A later calculation by McWeeny and Ohno[4] also included configuration interaction but was based on Ellison and Shull's inaccurate integral values. Merrifield[5] performed a more accurate calculation by using an extended basis set and by independently

evaluating molecular integrals; his work has not yet been completed, however.

Although not yet reported in the literature, approximate Hartree-Fock wavefunctions for several molecular geometries of the water molecule have been obtained by Pitzer and Merrifield[6] using a minimal basis set of Slater-type atomic orbitals with optimized exponents. They calculated the dipole moment, the vibrational force constants, and the equilibrium molecular geometry, finding good agreement with experiment.

Recently, calculation of the electric polarizability of the water molecule using Hartree-Fock perturbation theory was reported by Arrighini, Maestro, and Moccia.[7] A large number of multicenter Slater-type basis functions were used. The calculations were based on unpublished molecular wavefunctions and integral values obtained by Salvetti and co-workers. The average polarizability calculated with their largest basis set agreed well with experiment.

All the foregoing calculations were based on multicenter Slater-type basis functions. Beginning in about 1964, a number of investigators turned toward the use of gaussian basis functions. Krauss[8] was interested in determining the equilibrium molecular geometry. Employing a medium-sized set of gaussian basis functions, he obtained a total molecular energy slightly superior to that obtained by Boys et al. who used eight Slater-type basis functions and included configuration interaction as mentioned above. The calculated equilibrium molecular geometry agreed very well with experiment.

Moskowitz and Harrison,[9] as well as Ritchie and King,[10] obtained the lowest theoretical total energies so far reported in the literature for the water molecule by using large sets of gaussian basis functions. Of these two groups of workers, Moskowitz and Harrison obtained a slightly lower total molecular energy and also reported a calculated dipole moment in good agreement with experiment.

Very recently, a number of one-electron properties of the water molecule have been calculated by J. F. Harrison[11] using unpublished wavefunctions obtained by Fink, Whitten, and Allen. The basis sets employed were small in size and consisted of gaussian lobe functions. The calculated dipole moment agreed rather poorly with experimental measurement.

In addition to the above multicenter calculations, several single-center wavefunctions for the water molecule have also been reported. Moccia[12] employed a large number of Slater orbitals centered on the oxygen nucleus while Bishop and Randic[13] used a smaller number of basis functions but included configuration interaction. Moccia obtained better agreement with experiment for the calculated total molecular energy, the equilibrium molecular geometry, and vibrational force constants. He also calculated the dipole moment, reporting good agreement with experiment.

Thus, essentially three kinds of basis functions have been employed in previous calculations of the ground-state electronic wavefunction of the water molecule. Single-center wavefunctions possess inherent theoretical limitations which have been discussed by

Moccia.[14] Such wavefunctions are expected to give a particularly unreliable description of the molecular electronic charge distribution in the vicinity of nuclei located away from the center of expansion. The most appropriate basis functions to use in calculating molecular electronic wavefunctions are therefore the multicenter functions. From the results of previous calculations discussed in the foregoing paragraphs, the number of individual multicenter gaussian and Slater-type basis functions required to achieve the same variational energy for the water molecule would be in the approximate ratio 4:1. Thus, previous calculations on the ground electronic state of the water molecule show that multicenter Slater-type basis functions provide by far the most compact analytic representation of the unperturbed molecular electronic wavefunction.

Finally, we mention two calculations which have been reported on excited electronic states of the water molecule. The first calculation is by La Paglia[15] and the second by Lin and Duncan.[16] Both calculations were motivated by the known Rydberg term values of the water molecule. The calculations are based on approximate Hartree-Fock wavefunctions for the ground state molecule and assume that excitation of the Rydberg electron does not affect the other electrons which thus remain in the ground state molecular orbitals. Useful results were obtained. They are not quantitatively reliable, however, since some approximations were made in the Hartree-Fock equation for the Rydberg orbital. In addition, La Paglia based his calculations on the inaccurate ground state wavefunction of Ellison and Shull,

while Lin and Duncan approximated the nuclear potential for the Rydberg electron.

1.2 Experimental measurements on the water molecule

After summarizing previous theoretical investigations of the water molecule, a brief discussion will now be given on experimental measurements since the verification of any theoretical calculation ultimately depends on experimental observation.

1.2.1 Properties measured

Experimental data exists for a large number of bulk properties of water in the liquid, vapour and solid states. These include the heat capacity,[17] the dielectric constant,[18] the second and third virial coefficients,[19] the Joule-Thompson coefficient,[20] the viscosity,[21] the Verdet constant,[22] and the surface tension in air.[23]

These bulk properties depend on the properties of the individual molecules and the intermolecular potential function via the theories of statistical mechanics. Properties which are characteristic of the individual water molecules and which have been measured to various degrees of accuracy are listed in Table I together with the methods used in the measurements.

1.2.2 Problems involved in some of the measurements

Measurement of the various molecular properties of water is by no means an easy task. Specifically, we cite the problems involved in measuring the ^{17}O quadrupole coupling constants and the molecular quadrupole moment, thus pointing out the importance of the alternative approach of theoretical calculation.

Table I. Properties measured for the water molecule

Property	Method of measurement [a]	Ref.
Ionization potentials	EI	24
Molecular structure, harmonic and anharmonic vibrational constants, centrifugal distortion coefficients, and rotation-vibration interaction constants	Fine structure of IR bands	25
Nuclear quadrupole coupling constants and spin-rotation interaction constants at the D nucleus	Hyperfine structure of MW spectrum; beam maser spectroscopy	26, 27, 28
Nuclear quadrupole coupling constants and effective spin-rotation interaction constant at the ^{17}O nucleus	Conventional MW spectroscopy	29
Magnetic shieldings at the H and ^{17}O nuclei	NMR	30, 31
Electric dipole moment	MW Stark effect	32
Rotational magnetic moment	MW Zeeman effect	33
Magnetic susceptibility	Modified Quincke balance	34, 35
Electric polarizability	Refractive index extrapolation	36
H-D and H-^{17}O nuclear spin-spin isotropic coupling constants	NMR	37, 31
Term values of Rydberg states	EI and vacuum-UV spectroscopy	38, 39
Molecular structure of the $(a_1)^2 (a_1)^2 (b_2)^2 (a_1)^2 (b_1) (3pa_1)$, $^1B_1$ Rydberg state	Vacuum-UV spectroscopy	39

[a] EI: electron impact
MW: microwave
UV: ultraviolet
IR: infrared
NMR: nuclear magnetic resonance

The ^{17}O quadrupole coupling constants were measured by using a conventional microwave spectrometer. The ^{16}O nucleus does not possess a quadrupole moment and the experiment was performed on HDO vapour containing ^{17}O isotopic species in low natural abundance. Furthermore, the water molecule is an asymmetric rotor and is not easily subjected to study through microwave spectroscopy. The measured ^{17}O quadrupole coupling constants were based on the $2_{20} \leftarrow 2_{21}$ rotational transition of $HD^{17}O$. The observed spectrum was poorly resolved. The derived ^{17}O quadrupole coupling constants gave a value for the field gradient asymmetry parameter that corresponds[29] to an unusually high s hybridization of 38% in the oxygen bonding orbitals of water according to the Townes-Dailey theory.[40] This led the investigators to conclude that the structure of bonds involving oxygen needs reexamination. From the foregoing considerations, there is clearly a need for an ab initio calculation of the field gradient at the oxygen nucleus in the water molecule.

Measurement of the molecular quadrupole moment of water would apparently be even more difficult than that of the ^{17}O quadrupole coupling constants. The magnitudes and signs of molecular quadrupole moments can be measured directly by the electro-optical method of Buckingham.[41] The quadrupole moment of a molecule with a vanishing dipole moment is independent of coordinate origin. For a dipolar molecule, Buckingham and Longuet-Higgins[42] have recently shown that contrary to earlier expectations, the coordinate origin of the molecular quadrupole moment measured in the *electro-optical*

experiment is not the molecular center of mass and, in fact, may not be easily determined, being dependent in a complicated manner on the optical frequency used in the measurement. Since knowledge of the coordinate origins, the signs, and the magnitudes of multipole moments is needed in specifying molecular fields, the direct measurement of the higher multipole moments of molecules must be regarded as an unsolved problem at the present time. Therefore, theoretical calculation of the molecular quadrupole and octopole moments of the water molecule is a timely step to pursue.

1.3 Scope of this thesis research

With such a wealth of experimental data and also a lack of it in some cases, it is highly desirable for a theoretical investigation of the water molecule to emphasize the ab initio calculation of its molecular properties. In section 1.1, previous ab initio calculations on the water molecule were summarized. As stated therein, good total molecular energies for the ground electronic state were obtained. However, few molecular properties were calculated. It has been pointed out [43] that a good total molecular energy does not necessarily imply a satisfactory description of the charge distribution in the molecule.

In the thesis research reported herein, several approximate Hartree-Fock self-consistent-field wavefunctions for the ground electronic state of the water molecule have been obtained using an increasing number of multicenter s, p and d Slater-type atomic orbitals as basis sets. At each stage, the electric dipole moment,

molecular quadrupole moment, diamagnetic shielding, Hellmann-Feynman forces, and electric field gradients at both the hydrogen and the oxygen nuclei have been calculated and compared with available experimental measurements. This comparison furnishes an extensive quantitative test of the predicted charge distribution since the one-electron properties calculated depend on different powers of the electron coordinate ranging from r^{-3} to r^{3}. Our calculated results are also compared with those calculated by Neumann and Moskowitz[44] who independently investigated the water molecule using very large sets of gaussian basis functions and whose work came to our attention at the conclusion of our own investigation. As the final steps in our research, the charge distribution predicted by our most elaborate wavefunction is plotted out pictorially in the form of contour maps, and the nature of the chemical bond in the water molecule is discussed in terms of the Townes-Dailey theory of nuclear quadrupole interaction in molecules.

2. Hartree-Fock theory

We briefly describe here the elements of molecular Hartree-Fock theory.[45]

In molecular Hartree-Fock theory, the Born-Oppenheimer separability of nuclear and electronic motions[46] is first assumed. The many-electron wavefunction for a closed-shell system is then taken to be an antisymmetrized product of one-electron molecular spinorbitals which satisfies the Pauli Principle. The expectation value of the electronic Hamiltonian is next obtained in terms of spatial integrals of molecular orbitals after integrating trivially over the spin factors. To this is applied the variational principle under the constraint that the molecular orbitals remain orthonormal. The resulting Hartree-Fock equations for the molecular orbitals are

$$F\phi_i = \epsilon_i \phi_i \qquad (2\text{-}1)$$

where F is a one-electron operator called the Hartree-Fock operator and is effectively the one-electron Hamiltonian governing the motion of an electron moving in the average field of all the other electrons. The eigenvalue ϵ_i is called the Hartree-Fock orbital energy corresponding to the ith molecular orbital ϕ_i.

In the approximate molecular Hartree-Fock theory first given a rigorous mathematical framework by Roothaan,[45] each molecular orbital ϕ_i is approximated by a finite linear combination of atomic orbitals χ_p:

$$\phi_i = \sum_{p=1}^{m} C_{pi}\, \chi_p, \qquad m \geq n \tag{2-2}$$

The matrix Hartree-Fock equations that result are

$$\underset{\sim}{F}\,\underset{\sim}{C} = \epsilon\,\underset{\sim}{S}\,\underset{\sim}{C} \tag{2-3}$$

where $S_{pq} = \int \chi_p^*\, \chi_q\, d\tau$

$$F_{pq} = \int \chi_p^* \left[h + \sum_i (2J_i - K_i)\right] \chi_q\, d\tau$$

$$\int \chi_p^* J_i\, \chi_q\, d\tau = \sum \iint \chi_p^*(1)\, \chi_q(1)\, \frac{1}{r_{12}}\, \phi_i^*(2)\, \phi_i(2)\, d\tau_1\, d\tau_2$$

$$\int \chi_p^* K_i\, \chi_q\, d\tau = \sum \iint \chi_p^*(1)\, \phi_i(1)\, \frac{1}{r_{12}}\, \phi_i^*(2)\, \chi_q(2)\, d\tau_1\, d\tau_2$$

and h is the Hamiltonian operator for an electron moving in the field of the bare nuclei.

The matrix $\underset{\sim}{C}$ is solved for numerically by the method of trial and error until a self-consistent solution is obtained.

3. Wavefunctions for the water molecule

3.1 Computer programs

In the present thesis research, four approximate Hartree-Fock SCF wavefunctions for the water molecule have been calculated using an increasing number of multicenter s, p, and d Slater-type atomic orbitals as basis sets. The computer programs written by R. M. Pitzer, J. P. Wright, W. E. Palke, D. E. Ellis, and C. A. Christy[47] have been employed after some modifications. The programs will henceforth be referred to as the Cambridge programs. A few errors in these extensive and painstakingly detailed programs were found and corrected. These errors do not, however, affect any published results based on the programs and therefore need not be elaborated on any further.

Most of these programs compute multicenter integrals by expanding each part of the integrand in terms of functions located on one of the centers. The expansion is done in such a way that angular integrations reduce any multiple infinite series to a single infinite series or to a finite number of terms. The systematic development of this procedure hinges on four basic steps.

The first step is the generation of rotation matrices for expressing real spherical harmonics (angular parts of Slater-type atomic orbitals) defined in one coordinate system in terms of real spherical harmonics defined in a rotated coordinate system.

If unprimed coordinates refer to one right-handed coordinate system while primed ones refer to another right-handed system rotated from the first through the Eurelian angles α, β, and γ as defined in Hirschfelder et al.,[48] then

$$P_\ell^n(\cos\theta)\, S_n^\sigma(\phi) = \sum_{m=0}^{\ell} \sum_{\sigma'=0}^{1} D_{nm}^{\ell\sigma\sigma'}\, P_\ell^m(\cos\theta')\, S_m^{\sigma'}(\phi') \qquad (3\text{-}1)$$

where $n \geq 0$

$$P_\ell^n(\cos\theta) = \frac{(\sin\theta)^n}{2^\ell\, \ell!} \left(\frac{d}{d\cos\theta}\right)^{\ell+n} (\cos^2\theta - 1)^\ell$$

$$S_n^\sigma(\phi) = \begin{cases} \cos n\phi, & \sigma = 0 \\ \sin n\phi, & \sigma = 1 \end{cases}$$

and

$$D_{nm}^{\ell\sigma\sigma'} = (-)^{n+m} \sqrt{\frac{(\ell+n)!\,(\ell-m)!}{(\ell-n)!\,(\ell+m)!}}\ \frac{2-\delta_{mo}}{2}$$

$$\left[(-)^{\sigma'} S_n^\sigma(\alpha)\, S_m^{\sigma'}(\gamma)\, d_{nm}^{+} + (-)^{1-\sigma} S_n^{1-\sigma}(\alpha)\, S_m^{1-\sigma'}(\gamma)\, d_{nm}^{-}\right]$$

with $$d_{nm}^{\pm} = d^\ell(\beta)_{nm} \pm (-)^{\ell+m+n}\, d^\ell(\pi-\beta)_{nm}$$

$d^\ell(\beta)_{nm}$ is the unnormalized Jacobi polynomial in $\cos\beta$ as given by Hirshfelder et al.[49]

If one or both coordinate systems have the polar axis reversed in direction so that spherical harmonics in one or both systems are now referred to a left-handed coordinate system, then the coefficient $D_{nm}^{\ell\sigma\sigma'}$ in (3-1) must be multiplied by one or both of the factors $(-)^{\ell+n}$ and $(-)^{\ell+m}$ since

$$P_\ell^{|k|}(-\cos\theta) = (-)^{\ell+k} P_\ell^{|k|}(\cos\theta)$$

By means of the rotation matrices, all molecular integrals involving three centers or less can now be referred to the standard coordinate systems of Figure 1 for which integrals are actually computed.

The second basic step in the Cambridge programs for multi-center integrals is the expansion of a real spherical harmonic on one center in terms of real spherical harmonics referred to a new coordinate system, obtained from the first by a translation along the polar axis followed by an inversion of the polar axis:

$$r_B^\ell P_\ell^{|m|}(\cos\theta_B)\, S_{|m|}^{\sigma}(\phi) =$$

$$\sum_{k=|m|}^{\ell} (-)^{k+m} \frac{(|m|+\ell)!}{(|m|+k)!\,(\ell-k)!} R^{\ell-k} r_A^k P_k^{|m|}(\cos\theta_A)\, S_{|m|}^{\sigma}(\phi) \qquad (3\text{-}2)$$

where R is the distance between centers A and B and r_A, r_B, θ_A, θ_B, and ϕ are spherical coordinates in the coordinate systems shown in Figure 2.

The third step is the expansion of the radial part of a Slater orbital on one center in terms of zeta functions and Legendre polynomials on another center:[51]

$$(k r_B)^{n-1} e^{-kr_B} = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-k|r_A-R|} \bar{\xi}_{n,\ell}(kr_A, kR) P_\ell(\cos \theta_A) \tag{3-3}$$

where the notation is that of Figure 2.

The zeta functions $\bar{\xi}_{n,\ell}(k r_A, k R)$ are identical to those of Barnett and Coulson[51] except for a scale factor. They are generated by an improved procedure due to R. M. Pitzer.[52] In this procedure, all zeta functions are assembled directly from Bessel functions without the use of recursion relations on the zeta functions themselves. This change in procedure gives improved accuracy particularly for the higher order zeta functions.

Finally, the fourth basic step in the Cambridge programs is the multipole expansion of the electron repulsion potential. When the number of different centers in the integrand is three or less, the form

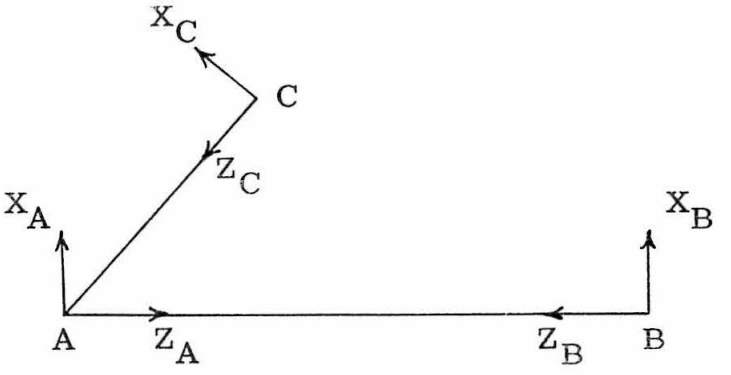


Figure 1. Actual coordinate system for which molecular integrals are computed. All three y axes point up from the plane of the paper. Hence the coordinate systems on centers B and C are left-handed.

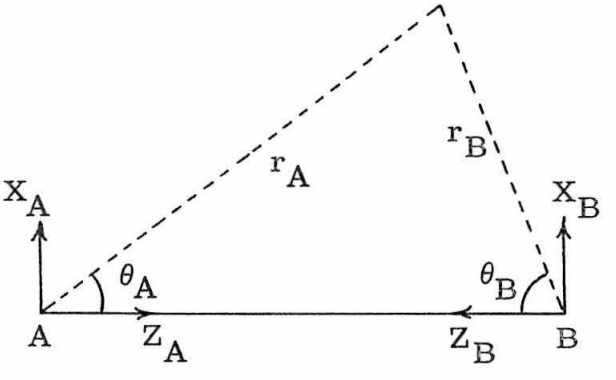


Figure 2. Coordinate systems used in defining the change in origin of a Slater-type atomic orbital.

used for the expansion is [53]

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}} \left[P_\ell(\cos\theta_1)\, P_\ell(\cos\theta_2) + 2 \sum_{m=1}^{\ell} \frac{(\ell-m)!}{(\ell+m)!}\, P_\ell^m(\cos\theta_1)\, P_\ell^m(\cos\theta_2) \cdot \cos m(\phi_1 - \phi_2) \right] \tag{3-4}$$

where r_{12} is the distance between the two electrons and $r_<$ and $r_>$ are respectively the smaller and the greater of r_1 and r_2. (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2) are the spherical coordinates of electrons 1 and 2, respectively, referred to the same origin.

This expansion is also used for off-center nuclear attraction potentials, with a nucleus replacing one of the electrons.

3.2 Calculations

In Hartree-Fock calculations, radial integrals by far take up most of the computing time. Each set of p or d atomic orbitals on each center have therefore been given the same exponent in this work. Clearly, several such sets of p or d atomic orbitals must be used in order to have much flexibility in describing non-spherical charge distribution.

Throughout this work, the experimentally determined equilibrium OH bond length of 1.8111 a.u. and $\hat{HOH}$ bond angle of 104°27' for the water molecule [54] have been assumed. This same molecular geometry has been used in all the relevant experimental work quoted herein for comparison with our calculations. The coordinate axes x,

y, and z on all centers point in the directions shown in Figure 3.

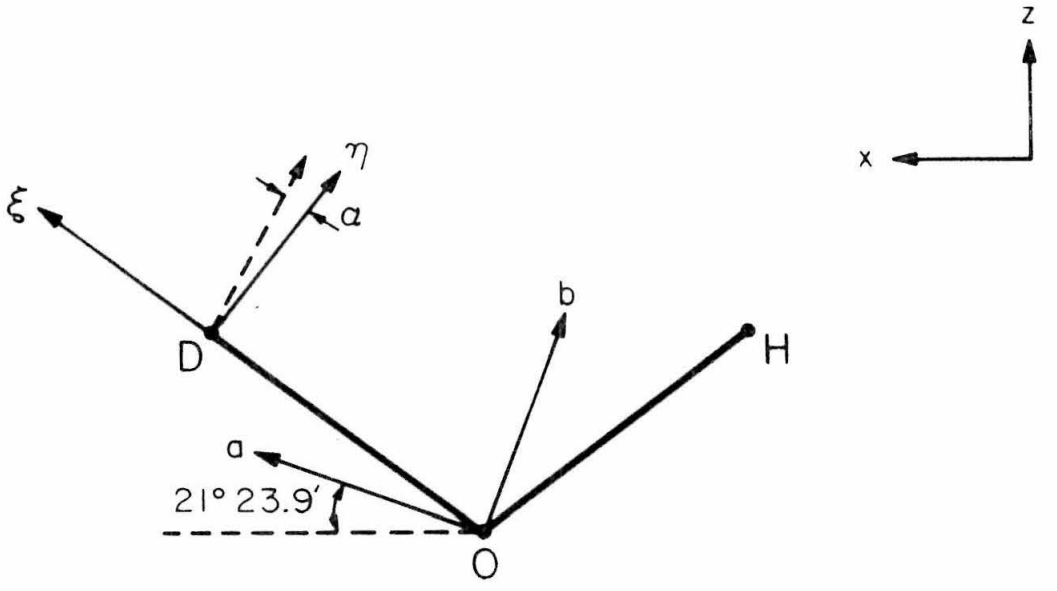


Figure 3. Coordinate axes employed in the calculation of the wavefunctions and properties of the water molecule. The z axis is parallel to the bisector of the $D\hat{O}H$ bond angle and the y axis points up from the plane of the molecule.

Values of the fundamental constants are taken from Cohen and DuMond's recent work.[55]

Four SCF electronic wavefunctions were calculated in this work. The wavefunctions are labelled I, II, III, and IV in order of increasing basis-set size (7, 10, 17, and 26 basis functions, respectively). Wavefunction I is one of several obtained by Pitzer and Merrifield[6] and corresponds to the minimal basis set. An additional set of 2p

orbitals on the oxygen nucleus was included in wavefunction II. III differs from II by an additional 1s orbital on each hydrogen nucleus, and a 2s and a set of 3d orbitals on the oxygen nucleus. Finally, wavefunction IV included an additional set of 2p orbitals on each center.

The evaluation of molecular integrals took approximately 4 minutes, $7\frac{1}{2}$ minutes, 35 minutes, and 3 hours for wavefunctions I, II, III, and IV, respectively. All computations were done on the IBM 7094 computer at Caltech. Orbital exponents were optimized in only the smaller wavefunctions I and II. It is interesting to note that only minor changes occur in optimal exponents of the oxygen orbitals from those of the free oxygen atom upon bond formation. This can be seen in Table II, where we compare the optimal exponents of the oxygen orbitals in wavefunctions I and II with those obtained using similar basis sets for the oxygen atom in the ^3P ground state. The atomic results for the minimal basis set (set A) are from the work of Clementi and Raimondi.[56] Those of the more extensive set (set B) have been calculated in these laboratories using the Atomic SCF Program Number 3 of Roothaan and Bagus.[57]

Table III lists the orbital exponents used for the atomic orbitals in wavefunctions III and IV. Several of these exponents were taken from our optimized wavefunction II but, as a whole, they were based on Cade and Huo's work on the OH radical[58] after scaling the optimized values in the OH wavefunction according to the ratio of the OH bond lengths. This procedure is probably justified since for Slater orbitals the distance of the radial maximum from the nuclear center

Table II. Comparison of optimal orbital exponents of the oxygen orbitals in two similar approximate Hartree-Fock wavefunctions for the ^3P oxygen atom and in the water molecule.

	Atom	Molecule
Set A		
1s	7.6579	7.66
2s	2.2458	2.25
2p	2.2266	2.21
Set B		
1s	7.65	7.65
2s	2.26	2.26
2p	1.66	1.56
2p′	3.69	3.60

Table III. Criteria for the orbital exponent values used in wavefunctions III and IV.

Orbital	Wavefunction III		Wavefunction IV	
	Exponent	Criterion	Exponent	Criterion
$1s_H$	1.33	C–H [a]	1.40	arbitrary
$1s'_H$	2.47	C–H		
$2s_H$			2.33	C–H
$2p_H$			1.85	C–H [c]
$1s_O$	7.65	II [b]	7.65	II
$2s_O$	1.74	C–H	1.74	C–H
$2s'_O$	2.90	C–H	2.90	C–H
$2p_O$	1.56	II	1.30	C–H
$2p'_O$	3.60	II	2.16	C–H
$2p''_O$			3.81	C–H
$3d_O$	1.66	C–H	1.66	C–H

[a] Cade and Huo's OH value multiplied by the bond length ratio $\frac{1.8342}{1.8111} = 1.01275$.

[b] Retained from wavefunction II.

[c] Based on the $\pi 2p_H$ orbital exponent in Cade and Huo's OH wavefunction.

is inversely proportional to the orbital exponent. In any case, since the OH bond lengths in water and the OH radical differ by less than 2%, the change in the orbital exponents is not expected to be large.

The futility of exponent optimization relative to increasing the basis-set size has been well established.[58] For example, in our case, for wavefunction II, exponent optimization took 5 hours of computer time producing only a small change of 0.014440 a.u. in energy. Here, the optimal exponents in atomic wavefunction B above and a hydrogen exponent of 1.27 were used as starting point for the optimization. The two sets of oxygen 2p orbitals were found to be strongly coupled together, necessitating double optimization of these two exponents in addition to single optimization of the other exponents. For wavefunctions III and IV, multiple optimizations would be even more important.

The basis functions, orbital exponents, molecular orbital coefficients, orbital energies, and total energies for all four wavefunctions are given in Tables IV to VII. A total of 34,266 non-vanishing integrals were needed in calculating wavefunction IV and it is therefore not practical to list the integral values here.

Table IV. Molecular orbital coefficients and energies for the water molecule: Wavefunction I.

Nucleus	Basis function[a]	Molecular orbital coefficients				
		$1a_1$	$2a_1$	$3a_1$	$1b_2$	$1b_1$
D	1s (1.27)	-0.003634	-0.151676	-0.264407	0.423525	0.
H	1s (1.27)	-0.003634	-0.151676	-0.264407	-0.423525	0.
O	1s (7.66)	0.996808	0.221858	-0.093444	0.	0.
	2s (2.25)	0.015189	-0.842535	0.515902	0.	0.
	$2p_z$ (2.21)	0.003159	-0.132019	-0.787220	0.	0.
	$2p_x$ (2.21)	0.	0.	0.	0.624043	0.
	$2p_y$ (2.21)	0.	0.	0.	0.	1.
Orbital energy[b]		-20.5559	-1.2850	-0.4661	-0.6242	-0.4026

Total energy = -75.703317

Kinetic energy = +75.746186

[a] Orbital exponents are given in parentheses.

[b] All energies are in a.u.

TABLE V. Molecular orbital coefficients and energies for the water molecule: Wavefunction II.

Nucleus	Basis Function[a]	Molecular Orbital Coefficients				
		$1a_1$	$2a_1$	$3a_1$	$1b_2$	$1b_1$
D	1s (1.50)	0.003658	-0.146790	0.160025	0.304599	0.
H	1s (1.50)	0.003658	-0.146790	0.160025	-0.304599	0.
O	1s (7.65)	-0.996661	0.224840	0.083515	0.	0.
	2s (2.26)	-0.015427	-0.857229	-0.410603	0.	0.
	$2p_z$ (1.56)	-0.002251	-0.104478	0.641687	0.	0.
	$2p_x$ (1.56)	0.	0.	0.	0.515880	0.
	$2p_y$ (1.56)	0.	0.	0.	0.	0.753116
	$2p'_z$ (3.60)	-0.001534	-0.060003	0.284225	0.	0.
	$2p'_x$ (3.60)	0.	0.	0.	0.270071	0.
	$2p'_y$ (3.60)	0.	0.	0.	0.	0.329345
Orbital energy[b]		-20.5421	-1.3534	-0.5638	-0.7099	-0.5077

Total energy = -75.969347
Kinetic energy = 75.927858

[a]Orbital exponents are given in parentheses.

[b]All energies are in a.u.

TABLE VI. Molecular orbital coefficients and energies for the water molecule: Wavefunction III.

Nucleus	Basis Function[a]		Molecular Orbital Coefficients				
			$1a_1$	$2a_1$	$3a_1$	$1b_2$	$1b_1$
D	1s	(1.33)	0.006306	0.018442	0.183026	0.179686	0.
	1s′	(2.47)	-0.002546	-0.081749	0.004649	0.049496	0.
H	1s	(1.33)	0.006306	0.018442	0.183027	-0.179686	0.
	1s′	(2.47)	-0.002546	-0.081749	0.004649	-0.049496	0.
O	1s	(7.65)	0.992712	0.232232	0.073543	0.	0.
	2s	(1.74)	-0.018319	-0.638333	-0.292621	0.	0.
	2s′	(2.90)	0.027634	-0.365527	-0.136794	0.	0.
	$2p_z$	(1.56)	-0.004232	-0.157274	0.627205	0.	0.
	$2p_x$	(1.56)	0.	0.	0.	0.592293	0.
	$2p_y$	(1.56)	0.	0.	0.	0.	0.752629
	$2p'_z$	(3.60)	0.003092	-0.030438	0.289972	0.	0.
	$2p'_x$	(3.60)	0.	0.	0.	0.255533	0.
	$2p'_y$	(3.60)	0.	0.	0.	0.	0.328185
	$3d_{3z^2-r^2}$	(1.66)	-0.000177	-0.011287	0.054568	0.	0.
	$3d_{zx}$	(1.66)	0.	0.	0.	0.103600	0.
	$3d_{x^2-y^2}$	(1.66)	-0.001558	-0.047446	0.006791	0.	0.
	$3d_{zy}$	(1.66)	0.	0.	0.	0.	0.053350
	$3d_{xy}$	(1.66)	0.	0.	0.	0.	0.
Orbital energy[b]			-20.5541	-1.3356	-0.5840	-0.7153	-0.5130

Total energy = -76.000440
Kinetic energy = 75.579000

[a]Orbital exponents are given in parentheses.

[b]All energies are in a.u.

TABLE VII. Molecular orbital coefficients and energies for the water molecule: Wavefunction IV.

Nucleus	Basis Function[a]		Molecular Orbital Coefficients				
			1a	2a	3a	$1b_2$	$1b_1$
D	1s	(1.40)	-0.002742	0.155823	0.178079	-0.288124	0.
	2s	(2.33)	0.002204	-0.009612	0.018268	-0.013111	0.
	$2p_z$	(1.85)	-0.001112	-0.020014	0.001162	0.028743	0.
	$2p_x$	(1.85)	-0.001095	-0.027048	-0.022159	0.020212	0.
	$2p_y$	(1.85)	0.	0.	0.	0.	0.026725
H	1s	(1.40)	-0.002742	0.155823	0.178079	0.288124	0.
	2s	(2.33)	0.002204	-0.009612	0.018268	0.013111	0.
	$2p_z$	(1.85)	-0.001112	-0.020014	0.001162	-0.028743	0.
	$2p_x$	(1.85)	0.001095	0.027048	0.022159	0.020212	0.
	$2p_y$	(1.85)	0.	0.	0.	0.	0.026725
O	1s	(7.65)	-0.993078	-0.239640	0.072220	0.	0.
	2s	(1.74)	0.010528	0.447181	-0.320504	0.	0.
	2s′	(2.90)	-0.025587	0.410713	-0.132111	0.	0.
	$2p_z$	(1.30)	0.001520	0.014437	0.364844	0.	0.
	$2p_x$	(1.30)	0.	0.	0.	-0.243358	0.
	$2p_y$	(1.30)	0.	0.	0.	0.	0.469982
	$2p'_z$	(2.16)	-0.001052	0.080842	0.323899	0.	0.
	$2p'_x$	(2.16)	0.	0.	0.	-0.338790	0.
	$2p'_y$	(2.16)	0.	0.	0.	0.	0.354678
	$2p''_z$	(3.81)	-0.001637	0.025196	0.219726	0.	0.
	$2p''_x$	(3.81)	0.	0.	0.	-0.190513	0.
	$2p''_y$	(3.81)	0.	0.	0.	0.	0.248775
	$3d_{3z^2-r^2}$	(1.66)	0.000238	0.007069	0.042325	0.	0.
	$3d_{zx}$	(1.66)	0.	0.	0.	-0.058474	0.
	$3d_{x^2-y^2}$	(1.66)	0.000329	0.018575	0.005437	0.	0.
	$3d_{zy}$	(1.66)	0.	0.	0.	0.	0.039069
	$3d_{xy}$	(1.66)	0.	0.	0.	0.	0.
Orbital energy[b]			-20.5654	-1.3392	-0.5950	-0.7283	-0.5211

Total energy = -76.004682
Kinetic energy = 75.662145

[a]Orbital exponents are given in parentheses.

[b]All energies are in a.u.

4. Electronic properties

4.1 Definitions and nature of one-electron properties

If P is a one-electron operator, then for a closed-shell system of 2n electrons, the expectation value of P according to a Hartree-Fock wavefunction is given by [59]

$$\langle P \rangle = 2 \sum_{i=1}^{n} \langle \phi_i | P | \phi_i \rangle \qquad (4\text{-}1)$$

where the molecular orbitals ϕ_i are defined in section 2 and the summation is over all occupied molecular orbitals.

The definitions of the one-electron properties calculated in this thesis for the water molecule are as follows in atomic units:

$$-q_{\alpha\beta}(N) = -\left\langle \frac{3 r_\alpha r_\beta - \delta_{\alpha\beta} r^2}{r^5} \right\rangle + \sum_k{}' Z_k \frac{3 r_{k\alpha} r_{k\beta} - \delta_{\alpha\beta} r_k^2}{r_k^5} \qquad (4\text{-}2)$$

Electronic contributions to the components of the Hellmann-Feynman force at nucleus N

$$f_\alpha(N) = Z_N \left\langle \frac{r_\alpha}{r^3} \right\rangle \qquad (4\text{-}3)$$

Average diamagnetic shielding at nucleus N

$$\sigma^d(N) = \frac{e^2}{3mc^2} \left\langle \frac{1}{r} \right\rangle \qquad (4\text{-}4)$$

Dipole moment

$$\vec{\mu} = -\langle \vec{r} \rangle + \sum_k Z_k \vec{r}_k \qquad (4\text{-}5)$$

Molecular quadrupole moment tensor components

$$\Theta_{\alpha\beta} = -\frac{1}{2}\langle 3\, r_\alpha r_\beta - \delta_{\alpha\beta} r^2 \rangle + \frac{1}{2}\sum_k Z_k (3\, r_{k\alpha} r_{k\beta} - \delta_{\alpha\beta} r_k^2) \quad (4\text{-}6)$$

Molecular octopole moment tensor components

$$\Omega_{\alpha\beta\gamma} = -\frac{1}{2}\langle 5\, r_\alpha r_\beta r_\gamma - r^2 (r_\alpha \delta_{\beta\gamma} + r_\beta \delta_{\gamma\alpha} + r_\gamma \delta_{\alpha\beta}) \rangle$$

$$+ \frac{1}{2}\sum_k Z_k \; 5\, r_{k\alpha} r_{k\beta} r_{k\gamma} - r_k^2 (r_{k\alpha} \delta_{\beta\gamma} + r_{k\beta} \delta_{\gamma\alpha} + r_{k\gamma} \delta_{\alpha\beta}) \quad (4\text{-}7)$$

Third moment tensor components

$$R_{\alpha\beta\gamma} = -\langle r_\alpha r_\beta r_\gamma \rangle + \sum_k Z_k (r_{k\alpha} r_{k\beta} r_{k\gamma}) \quad (4\text{-}8)$$

In the above definitions, Greek indices are used to denote cartesian components of vectors and tensors. Thus, r_α is a cartesian component of the vector $\vec{r}$, the integration variable, while $r_{k\alpha}$ is a cartesian coordinate of the position vector $\vec{r}_k$ of nucleus k with charge Z_k. $\delta_{\alpha\beta}$ is the Kronecka delta. e and m are respectively the electron charge and mass while c is the velocity of light. $q_{\alpha\beta}$ is by convention[60] the second derivative of the electrostatic potential with respect to the α and β position coordinates and hence $-q_{\alpha\beta}$ is the corresponding field gradient component. The coordinate origin of the field gradient, Hellmann-Feynman force and average diamagnetic shielding operators is to be taken at the specified nucleus, N, indicated in parentheses. The index k runs over all the nuclei except that a prime on the

summation symbol indicates omission of the nucleus to which the one-electron property is referred as origin.

The first non-vanishing multipole moment of the water molecule is the dipole moment which is therefore independent of coordinate origin. The quadrupole and octopole moments have been defined according to Buckingham [41] and will be referred to the center of mass of $H_2{}^{16}O$ as origin in the present calculations. Enough information will, however, be provided in this thesis to allow a translation to any other coordinate origin.

The nature of some of the one-electron properties will now be discussed.

The electric field gradient tensor appears in the expression for the energy of electrostatic interaction between electrons and a nucleus possessing a nuclear quadrupole moment. The zero order energy is that due to coulombic interaction between electrons and a point charge nucleus. Higher order corrections appear in the multipole expansion of the electron-nuclear electrostatic potential.[53] These corrections arise physically from the finite spatial distribution of the nuclear charge, the lowest order correction being the nuclear quadrupole interaction energy. For the case of an asymmetric top molecule containing a nucleus with a quadrupole moment, the expectation value of the nuclear quadrupole interaction Hamiltonian in a given rotational state may be reduced to the following convenient form: [60]

$$W_Q = \frac{1}{2} \cdot \frac{|e| q_J Q}{I(2I-1)\,J(2J-1)} \left[\frac{3}{4} C(C+1) - I(I+1)\,J(J+1) \right] \qquad (4\text{-}9)$$

where |e| is the proton charge, I the nuclear spin quantum number, and J the quantum number of total rotational angular momentum of the molecule including nuclei and electrons. The remaining symbols have the following meanings.

$$C = F(F+1) - I(I+1) - J(J+1); \qquad \vec{F} = \vec{I} + \vec{J}$$

$$q_J = \frac{q_{aa}}{(J+1)(2J+3)}\left[J(J+1) + E(\kappa) - (\kappa+1)\frac{\partial E(\kappa)}{\partial \kappa}\right]$$

$$+ \frac{2\,q_{bb}}{(J+1)(2J+3)}\frac{\partial E(\kappa)}{\partial \kappa}$$

$$+ \frac{q_{cc}}{(J+1)(2J+3)}\left[J(J+1) - E(\kappa) + (\kappa-1)\frac{\partial E(\kappa)}{\partial \kappa}\right]$$

$$Q = \frac{1}{|e|}\int \rho_n(\vec{r}_n)\,(3\,z_n^2 - r_n^2)\,d\vec{r}_n$$

Here, q_{aa}, q_{bb}, and q_{cc} are as defined in (4-2), a, b, and c being the principal axes of inertia of the molecule in order of decreasing rotational constants, κ is Ray's asymmetry parameter of the asymmetric rotor [61] and $E(\kappa)$ the well documented reduced rotational energy of an asymmetric rotor with rotational constants 1, κ, and -1.[60, 62] $E(\kappa)$, and hence q_J, is a function of the rotational state. Q is called the nuclear quadrupole moment. $\rho_n(\vec{r}_n)$ is the nuclear charge density at the position $\vec{r}_n$ referred to the nuclear charge centroid as origin. z_n is the component of $\vec{r}_n$ along the direction of $\vec{I}$, and $d\vec{r}_n$ the volume element of integration over all space.

The separations between nuclear quadrupole interaction energy levels are generally of the order of microwave and radio frequencies and have therefore been quite commonly observed under various degrees of spectroscopic resolution. Experimental results obtained via microwave spectroscopy are usually reported in terms of values for the quantities $|e|q_{aa}Q$, $|e|q_{bb}Q$, etc. which are called the nuclear quadrupole coupling constants and are conventionally denoted as χ_{aa}, χ_{bb}, etc.

From the definitions, it can be seen that all field gradient components will vanish for a spherical charge distribution. The field gradient at an atomic nucleus is therefore zero for s electrons and for a closed shell of p electrons. It will differ from zero when the effective number of p electrons around a nucleus is less than six. The relation of electric field gradient tensor components to hybridization and other aspects of chemical bonding in molecules is thus possible and forms an objective of the Townes-Dailey theory on which further discussion will be made in section 5.2.

According to the Hellmann-Feynman theorem,[63] we have

$$\frac{\partial E}{\partial \lambda} = \langle \psi | \frac{\partial H}{\partial \lambda} | \psi \rangle \qquad (4\text{-}10)$$

where ψ and E are respectively the electronic wavefunction and energy of a molecule at a fixed nuclear configuration obtained assuming the Born-Oppenheimer separability of nuclear and electronic motions. H is the total Hamiltonian of the system excluding the nuclear kinetic

energy terms, and λ is one of any number of parameters specifying nuclear positions in H, for example a nuclear position coordinate. The integration indicated in the right-hand-side expression is over the electronic coordinates.

The force on a nucleus defined by an increase in the nuclear coordinate R is $-\frac{\partial E}{\partial R}$. The actual evaluation of this quantity is based on the definition of a derivative as a limiting value and therefore the value of E at at least two neighbouring values of R must be known. This would involve the solution of Schrödinger's equation for the electronic wavefunction at at least two nuclear configurations. Application of the Hellmann-Feynman theorem, however, gives

$$-\frac{\partial E}{\partial R} = -\langle \psi | \frac{\partial H}{\partial R} | \psi \rangle \qquad (4\text{-}11)$$

showing that the same result can be obtained through knowledge of ψ at the single nuclear configuration of interest. The right-hand-side expression of (4-11) is called the Hellmann-Feynman force. It is identical to the expression for the electrostatic force that would be derived by assuming that the electronic charge distribution has the probability density $\psi^*\psi$. The Hellmann-Feynman theorem holds for the exact Hartree-Fock wavefunction for a closed-shell system, as well as for the exact wavefunction ψ.

Molecular multipole moments arise in the quantitative expression for molecular electric fields. In the field of a molecule, the electrostatic potential at a distant point $\vec{R}$ referred to some coordinate origin

within the molecule is given by[41]

$$\phi(\vec{R}) = -\mu_\alpha \frac{R_\alpha}{R^3} + \frac{1}{3}\Theta_{\alpha\beta}\frac{3R_\alpha R_\beta - \delta_{\alpha\beta}R^2}{R^5} - \frac{1}{5}\Omega_{\alpha\beta\gamma}\frac{5R_\alpha R_\beta R_\gamma - R^2(\delta_{\beta\gamma}R_\alpha + \delta_{\gamma\alpha}R_\beta + \delta_{\alpha\beta}R_\gamma)}{R^7} + \text{--------} \qquad (4\text{-}12)$$

where the multipole moments, defined earlier in this section, have the same coordinate origin as the vector $\vec{R}$. The indices α, β, and γ stand for cartesian components of vectors and tensors, and summation is implied over repeated indices in accordance with the Einstein summation convention.[64]

Given the multipole moments of two polar molecules, a major contribution to the long-range intermolecular potential is in principle determined. In the case of the water molecule, although the dipole moment is large and the contributions of higher moments to the molecular electric field decrease with the distance R, these higher moments may not be negligible in the intermolecular potential function. For example, the third virial coefficient of steam has been evaluated taking dipole-dipole interaction into account.[65] Distinct disagreement between calculated and experimental values was found and has been attributed to the neglect of higher multipole moments, in particular the dipole-quadrupole interaction.

4.2 Computation of one-electron properties

If the LCAO expansion (2-2) is used to approximate the Hartree-Fock molecular orbitals in (4-1), the expectation value of a one-electron operator P for a closed-shell system of 2n electrons becomes

$$\langle P \rangle = 2 \sum_{p=1}^{m} \sum_{q=1}^{m} C_{pi} C_{qi} \langle \chi_p | P | \chi_q \rangle$$

$$= 2 \, \mathrm{Tr} \, (\underset{\sim}{C}^t \underset{\sim}{P} \underset{\sim}{C}) \qquad (4\text{-}13)$$

where $\underset{\sim}{C}^t$ is the transpose of the matrix $\underset{\sim}{C}$, P is the matrix with elements $P_{pq} = \langle \chi_p | P | \chi_q \rangle$, and Tr indicates the trace of a matrix product.

A computer program for calculating the multicenter matrix elements P_{pq} for the diamagnetic shielding, force and field gradient operators between s and p Slater-type orbitals has been described previously.[66] We have added several subroutines, one due to W. E. Palke, so that all necessary rotations and labelling can be done completely automatically to minimize errors. For calculating integrals of all the one-electron operators involving d-orbitals, the existing Cambridge computer program (see section 3.1) used in calculating three- and two-center coulomb integrals was suitably modified as explained below.

The three-center coulomb integral is defined as

$$\mathrm{AABC} = \iint A(1) \, A(1) \, \frac{1}{r_{12}} \, B(2) \, C(2) \, d\tau_1 \, d\tau_2$$

$$= \int V_A(2) \, B(2) \, C(2) \, d\tau_2 \qquad (4\text{-}14)$$

where, for example, A(1) denotes an atomic orbital of electron 1 centered on A, VA(2) is the result of integrating over the coordinates of electron 1 and represents the coulomb potential felt by electron 2, and $d\tau_1$, $d\tau_2$ are the volume elements of integration.

In the existing Cambridge program for calculating AABC, the integration over electron 2 is done in the A coordinate system by expanding B(2) and C(2) in terms of zeta functions and real spherical harmonics centered on A. Thus, AABC may be converted into a three-center one-electron integral by replacing the function VA with a one-electron operator. If the angular part of A(1) A(1) is a product of two real spherical harmonics of orders ℓ_1 and ℓ_2, then by using the multipole expansion (3-4), VA(2) will be obtained as a linear combination of real spherical harmonics of electron 2 with orders $|\ell_1 - \ell_2|$ to $(\ell_1 + \ell_2)$. The correct angular dependence of the different one-electron operators is generated by the following values of ℓ_1 and ℓ_2:

ℓ_1	ℓ_2	Operator
0	0	1/r
0	1	Hellmann-Feynman force and dipole moment
0	2	Electric field gradient and molecular quadrupole moment (spherical tensor components)
1	1	Electric field gradient and molecular quadrupole moment (cartesian tensor components)
1	2	Molecular octopole moment

The conversion of AABC to an integral of a one-electron operator can thus be effected by modifying essentially only the radial part of the integration and the normalization constant. Two- and one-center integrals were obtained by making some changes in the original programs to make centers B and C collapsible onto A.

The computer program for two-center coulomb integrals AABB was modified in a similar manner. By comparing values for integrals of one-electron operators obtained with this program and those from the modified AABC program, an internal check of the two original programs as well as of the modified programs was obtained. This check turned out to be a highly valuable one.

These modified programs of course also work for s and p orbitals. An external check was thus possible by comparing integral values with those obtained by the program of R. M. Pitzer.[66] Values were found to agree to 10^{-6} a.u. or better.

To sum the slowly convergent infinite series encountered in the three-center programs when the operator is on the molecular axis, the non-linear sequence-to-sequence transformation described by Petersson and McKoy[67] was indeed found to be effective and was used after independent testing for accuracy. The dipole moment results were checked with a program written independently by M. D. Newton and F. P. Boer[68] for s and p orbitals, and integral values were found to agree to 10^{-6} a.u.

4.3 Results and comparison with experiment

Calculated values for the various electronic properties obtained with all four wavefunctions are shown in Table VIII. Experimental values where available are given for comparison.

In Table VIII, V, and T stand for potential and kinetic energies, respectively. Koopmans' Theorem [69] is invoked and the entries listed as calculated ionization potentials are just the negative of the three highest orbital energies associated with each wavefunction.

Field gradient components (a.u.) at the D nucleus have been transformed to the coordinate system with axes parallel and perpendicular to the OD bond (ξ, η in Figure 3) and converted into deuteron quadrupole coupling constants using the multiplication factor [70]

$$\frac{e^2Q(D)}{ha_0^3} \times 10^{-6} = 0.65713 \text{ Mc/a.u.}$$

for comparison with the experimental values of Posener [26] and Bluyssen et al.[27] α is the angle of rotation for diagonalization of the quadrupole coupling tensor at the deuteron (see Figure 3).

The field gradient components $-q_{xx}(O)$ and $-q_{zz}(O)$ at the oxygen nucleus were converted to values for the ^{17}O quadrupole coupling constant $\chi_{aa}(^{17}O)$ using a value of $Q(^{17}O) = -0.024$ barn for the ^{17}O quadrupole moment for comparison with Stevenson and Townes' experimental value.[29] The subscripts a, b, c refer to the principal inertial axes of $HD^{17}O$ (see Figure 3). $\eta(O)$ is defined as [29] $[q_{bb}(O) - q_{cc}(O)]/q_{aa}(O)$. The experimental value for $\chi_{ab}(^{17}O)$ was

TABLE VIII. Calculated and experimental energies and one-electron properties of the water molecule[a].

		I	II	III	IV	Experiment	Neumann-Moskowitz[b]
Total energy (hartrees)		-75.703317	-75.969347	-76.000440	-76.004682	-76.481[c]	-76.05936
-V/T		1.998868	2.001093	2.011152	2.009054	2.000000[d]	2.00066
Ionization potentials (a.u.)		0.4026	0.5077	0.5130	0.5211	0.463 ± 0.004[e]	0.5069
		0.4661	0.5638	0.5840	0.5950	0.533 ± 0.011[e]	0.5822
		0.6242	0.7099	0.7153	0.7283	0.595 ± 0.011[e]	0.7190
$\chi_{\xi\xi}(D)$	(Mc/sec)	0.3437	0.3888	0.3595	0.3626	0.3152 ± 0.0077[f]	0.3411
$\chi_{\xi\eta}(D)$	(Mc/sec)	-0.0204	-0.0270	-0.0041	-0.0085	-0.0088 ± 0.0087[f]	-0.0083
$\chi_{\eta\eta}(D)$	(Mc/sec)	-0.1502	-0.1741	-0.1588	-0.1586	-0.1393 ± 0.0070[f]	-0.1478
α		2°22′	2°44′	0°27′	0°57′	1°7′ ± 1°10′[f]	0°58′
$\chi_{aa}(^{17}O)$	(Mc/sec)	-11.584	-9.364	-9.072	-8.331	-8.13 ± 0.1[g]	-8.34
$\eta(O)$		1.547	1.525	1.550	1.484	0.7 ± 0.1[g]	1.506
$\chi_{ab}(^{17}O)$	(Mc/sec)	3.896	3.196	3.045	2.923	4.33[h]	2.88
$f_z(D)$	(a.u.)	-1.4776	-1.4586	-1.4620	-1.4975	-1.4940[i]	-1.505
$f_x(D)$	(a.u.)	-1.9778	-1.9401	-2.0136	-2.0482	-2.0498[i]	-2.081
$f_z(O)$	(a.u.)	0.1172	0.7946	2.6720	2.4261	2.9880[i]	2.928
$\sigma^d(D)$	(ppm)	103.6	101.7	102.1	102.0	102.0[j]	102.9
$\sigma^d(O)$	(ppm)	415.3	415.8	415.0	415.0		416.1
μ	(Debyes)	1.921	2.827	1.949	2.035	1.85 ± 0.02[k]	1.995
$\langle\sum_k r_{0k}^2\rangle$	(10^{-16} cm^2)	4.940	5.349	5.367	5.462	5.1 ± 0.7[ℓ]	5.371
Θ_{zz}	(10^{-26} esu.cm^2)	-0.008	-0.123	-0.053	-0.050		-0.108
Θ_{yy}	(10^{-26} esu.cm^2)	-1.485	-2.307	-2.496	-2.589		-2.422
Ω_{zzz}	(10^{-34} esu.cm^3)				-1.353		-1.337
Ω_{zyy}	(10^{-34} esu.cm^3)				-1.136		-0.960
R_{zxx}	(10^{-34} esu.cm^3)				1.325		1.191

Footnotes for Table VIII.

[a] For explanation of notations, see text. For each property, the relevant nuclear center is indicated in parentheses.

[b] Calculated by Neumann and Moskowitz with their best gaussian basis wavefunction, Ref. 44. Note that the molecular geometry assumed by these workers differs slightly from ours.

[c] Oxygen atomic energy (-75.1101 a.u.) from Ref. 58. Dissociation energies of O_2 and H_2 from P. Brix and G. Herzberg, Can. J. Phys. 32, 110 (1954) and G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950). Heat of formation of H_2O from Ref. 17. Zero-point energy of H_2O derived from data of Benedict, Gailar, and Plyler, Ref. 25.

[d] Exact value according to the virial theorem.

[e] Reference 24.

[f] References 26, 27.

[g] Reference 29.

[h] Derived from the experimental values of $\chi_{aa}(^{17}O)$ and $\eta(O)$.

[i] Nuclear contribution to the force as derived from the experimentally determined equilibrium molecular geometry.

[j] Based upon the spin-rotational constants of Ref. 28 and the equilibrium molecular geometry.

[k] Reference 32.

[l] Reference 35.

derived from Stevenson and Townes' values for $\chi_{aa}(^{17}O)$ and $\eta(O)$ using the symmetry relationship $q_{zx}(O) = 0$.

The quadrupole moment of ^{17}O adopted in this work is that due to Bessis et al.[71] A slightly different value has been reported by Kamper, Lea and Lustig.[72] In the latter work, $\langle \frac{1}{r^3} \rangle_{2p}$ and the quadrupole coupling constant were obtained from the e.s.r. spectrum of atomic oxygen, and these quantities were combined to yield a value of -0.0265 barn for the ^{17}O quadrupole moment after making allowance for the Sternheimer factor.[73] The value of Bessis et al. is based upon the observed quadrupole coupling constant for the $^3P_2$ state of atomic oxygen (-10.44 Mc/sec) and the electric field gradient calculated with their configuration-interaction wavefunction, without correcting for the Sternheimer effect. The reliability of Bessis et al.'s values of the quadrupole moment for the ^{17}O nucleus clearly depends upon the accuracy of the electric field gradient calculated with their configuration-interaction wavefunction. We have decided to use the value of Bessis et al. since their wavefunction also yields a value for $\langle 1/r^3 \rangle_{2p}$ which is in good agreement with experiment. In this connection, we have also computed $\langle 1/r^3 \rangle_{2p}$ and $\langle P_2^0/r^3 \rangle$ for the $^3P_2$ oxygen atom using the limited basis-set function A due to Clementi and Raimondi[56] and our atomic wavefunction B. The results of these calculations are compared with the values of Bessis et al. and with experiment in Table IX. It is interesting to note that while the expectation values obtained with the minimal basis set are in

Table IX. Calculated and experimental values of $\langle \frac{1}{r^3} \rangle_{2p}$ and $\langle \frac{P_2^0}{r^3} \rangle$ for the $^3P_2$ oxygen atom.[a]

	Wavefunction A[b]	Wavefunction B	Bessis et al.[c]	Experiment[d]
$\langle \frac{1}{r^3} \rangle_{2p}$ (10^{25} cm^{-3})	2.48	3.26	3.08	3.10
$\langle \frac{P_2^0}{r^3} \rangle$ (10^{25} cm^{-3})	-0.50	-0.65	-0.62	-0.62
$Q_{eff}(O^{17})$ (barn)	-0.030	-0.023	-0.024	-0.024

[a] The effective quadrupole moment $Q_{eff}(O^{17})$ is derived using the observed quadrupole coupling constant of -10.44 Mc/sec (Ref. 72, 74).

[b] Ref. 56.

[c] Ref. 71.

[d] Ref. 72, 74.

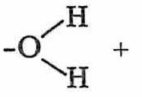
poor agreement with experiment, the results obtained with set B are in reasonable agreement with the calculations of Bessis et al. and with experiment. These results provide some indication of the accuracy in the computed field gradient of Bessis et al. Finally, we note that the paramagnetic resonance results of Kamper et al.,[72] as well as the more recent e.s.r. measurements of Harvey,[74] also yield an effective ^{17}O quadrupole moment of -0.024 barn when their deduced values of $\langle \frac{1}{r^3} \rangle_{2p}$ are combined with the observed ^{17}O quadrupole coupling constant.

The experimental value for $f_\alpha(N)$, the α component of the Hellmann-Feynman force exerted by all the electrons on nucleus N, is obtained by considering the contribution to the force by the other nuclei at the known experimental equilibrium geometry of the molecule.

The experimental value of the diamagnetic shielding at the proton is 102.0 ppm, and was determined using the well-known expression[75] relating the nuclear magnetic shielding constant and the spin-rotation interaction constants. The absolute proton shielding was obtained from the absolute magnetic shielding[76] in H_2 (26.6 ppm) and from the known chemical shift[30] (3.60 ppm) of gaseous H_2O relative to gaseous H_2. Several sets of spin-rotational constants for the proton in H_2O and HOD have been reported in the literature.[77, 78, 28] The best data appear to be those of Bluyssen et al.,[28] and we have used their reported spin-rotational constants in the evaluation of the paramagnetic part of the magnetic shielding.

No experimental value for the diamagnetic shielding at the oxygen nucleus is available.

The electric dipole moment μ is defined positive for



The sign has not been determined experimentally but is most certainly positive.

The quantity $\langle \sum_k r_{0k}^2 \rangle$ is the mean square distance of the electrons from the center of mass of $H_2{}^{16}O$. The quadrupole moment tensor Θ, the octopole moment tensor Ω and the third moment tensor R are all referred to the center of mass of the $H_2{}^{16}O$ molecule as origin.

In the last column of Table VIII, we have included for comparison with our calculated properties the recently calculated values of Neumann and Moskowitz [44] (after necessary conversions). These values are based upon their best gaussian wavefunction.

4.4 Discussion of results

4.4.1 Energies

The best total energy obtained in this work is about 0.47 a.u. higher than the experimental value. The energy calculated by Neumann and Moskowitz using their best gaussian wavefunction is somewhat better than ours, their value being lower by 0.05468 a.u. An energy drop of as much as 0.03 a.u. can be expected by including an additional $1s_O$ function in our present largest basis set.

The virial ratio -V/T should be exactly 2.0 for an exact wavefunction at the equilibrium molecular geometry as well as for an exact Hartree-Fock wavefunction at the Hartree-Fock equilibrium geometry. Both the lack of geometry variation and the lack of orbital exponent variation in wavefunctions III and IV are certainly reasons for the deviations from the theoretical value in our results. The use of the virial theorem as a criterion for judging wavefunction accuracy has been critically discussed by Fraga and Ransil.[79]

As first pointed out by Koopmans,[69] Hartree-Fock orbital energies should be good approximations to the vertical ionization potentials of a closed-shell atom or molecule. The vertical ionization potentials predicted for the water molecule in the present calculations using Koopmans' Theorem increase monotonically with basis-set size. This is hardly surprising since each time the molecular orbitals are given more freedom, the wavefunction is varied to get a minimal energy for the neutral molecule. However, the optimal molecular orbitals so determined are not necessarily optimal for the ionized molecule, whose energy therefore does not necessarily get lowered each time. The difference in correlation energies in the neutral and ionized molecules is independent of basis-set size. Thus an increasing gap between the two energy levels can be expected. In the case of water, because the ionization potentials predicted with the minimal-basis-set wavefunction are already fairly close to the experimental values, they tend to diverge from the latter values as more and more basis functions are added, contrary to the hope expressed by Ellison

and Shull[2] thirteen years ago.

4.4.2 One-electron properties

In Table VIII, it is seen that the minimal-basis-set wavefunction I describes the molecular electronic charge distribution well except in the vicinity of the oxygen nucleus. The force and the field gradient at the oxygen nucleus are off, but other one-electron properties agree with experimental data. Wavefunction II has a total energy lower than that of the minimal-basis-set one by about 0.27 a.u. (7 e.v.) but the calculated properties did not improve much. The dipole moment in particular turns out to be far too high. The importance of a balanced basis set is clearly demonstrated here. From the results listed in the work of Arrighini, Maestro, and Moccia[7] on the water molecule, it is also clear that 3d functions on the oxygen nucleus can be important in predicting the dipole moment. This point has been discussed by Mulliken.[43]

4.4.2.1 Oxygen field gradient

Agreement with the experimental value for the nuclear quadrupole coupling constant χ_{aa} for ^{17}O was achieved only with wavefunction IV. The biggest improvement in the calculated value for this quantity are seen to occur in going from I to II and from III to IV. This suggests that the correct prediction of field gradients at the ^{17}O nucleus requires a flexible linear combination of p functions centered on this nucleus. We noted that the d-orbitals included in wavefunctions III and IV contributed little to the calculated electric field gradient at the oxygen nucleus.

All four wavefunctions predict an asymmetry parameter η which is about twice the experimentally observed value.[29] Although the calculated electronic and nuclear contributions to each field gradient component at the deuteron nucleus are nearly equal in magnitude but opposite in sign, no loss of accuracy due to subtraction is possible for the oxygen field gradient since the nuclear and electronic contributions for this property have the same sign for each component. The electronic contributions to the one-electron operators are compared with the nuclear contributions in Tables Xa to Xc for the case of wavefunction IV. (For the sake of completeness, a breakdown of electronic contributions into contributions from each occupied molecular orbital has been included in the tables.)

Since q_{aa} is accurately predicted, it would seem that the disagreement for η between theory and experiment arises from an error in the calculated q_{bb} (or q_{cc}), or from uncertainties in the experimental value. We note that if q_{aa} is accurately determined and q_{bb} is in error, then this error will be magnified twofold in the calculated value of η, since the third component q_{cc} is determined from the trace condition. It is doubtful that vibrational averaging,[80, 81] additional basis functions, or a different form of the wavefunction such as a configuration-interaction wavefunction or the recently developed GI wavefunctions[82] would alter the theoretical values for $\eta(O)$ and $\chi_{ab}(^{17}O)$[83] to the necessary extent. For example, our calculated values for $\eta(O)$ and $\chi_{ab}(^{17}O)$ and those of Neumann and Moskowitz agree to about two significant figures. However, the $2_{20} \leftarrow 2_{21}$

Table Xa. Comparison of electronic and nuclear contributions to one-electron properties: Electric field gradients.[a]

Property	$-q_{zz}(D)$	$-q_{zx}(D)$	$-q_{xx}(D)$	$-q_{zz}(O)$	$-q_{xx}(O)$
$1a_1$	-0.042184	-0.489152	-0.294595	0.000919	0.001695
$2a_1$	0.040240	-0.346716	-0.308852	-0.163775	-0.009549
$3a_1$	0.052810	-0.144038	-0.250785	-5.310969	2.643117
$1b_2$	-0.185831	-0.354437	-0.051539	2.244247	-4.588175
$1b_1$	0.052007	-0.241018	-0.090067	3.341631	3.338944
Electronic contribution	-0.082958	-1.575361	-0.995838	0.112054	1.386033
Nuclear contribution	0.126664	1.956111	1.262620	0.042318	0.294350
Total	0.043707	0.380749	0.266781	0.154372	1.680384

[a] All values are in a.u.

Table Xb. Comparison of electronic and nuclear contributions to one-electron properties: Hellmann-Feynman forces and average diamagnetic shieldings.[a]

Property	f_z(D)	f_z(D)	f_z(O)	σ^d(H)	σ^d(O)
$1a_1$	-0.373511	-0.482112	0.343177	1.104426	15.18699
$2a_1$	-0.316506	-0.515743	2.238956	1.235302	2.32239
$3a_1$	-0.145807	-0.374381	-2.043296	1.050494	2.00872
$1b_2$	-0.422428	-0.352150	1.498799	1.376719	1.78721
$1b_1$	-0.239259	-0.323776	0.388431	0.977416	2.07619
Electronic contribution	-1.497512	-2.048162	2.426073	5.744356	23.38151
Nuclear contribution	0.	0.	0.	0.	0.
Total	-1.497512	2.048162	2.426073	5.744356	23.38151

[a] All values are in a.u.

Table Xc. Comparison of electronic and nuclear contributions to one-electron properties: Multipole moments.[a]

Property	μ	Θ_{zz}	Θ_{yy}	R_{zzz}	R_{zxx}	R_{zyy}
$1a_1$	-0.000683	-0.030657	0.015311	-0.016829	0.004354	0.004346
$2a_1$	-0.673678	-0.002103	0.355941	0.776643	-0.222367	-0.455212
$3a_1$	0.203651	-1.825047	1.128063	-0.513922	0.290377	-0.205665
$1b_2$	-0.789870	0.884363	1.461588	1.214701	-0.302474	-1.481272
$1b_1$	-0.157678	0.920456	-1.804128	-0.010714	0.009269	-0.038508
Electronic contribution	1.418259	-0.052988	1.156775	-1.449879	-0.220841	-2.176310
Nuclear contribution	2.218823	0.015478	3.081673	1.897498	0.	4.038132
Total	0.800565	-0.037509	-1.924898	0.447619	-0.220841	1.861822

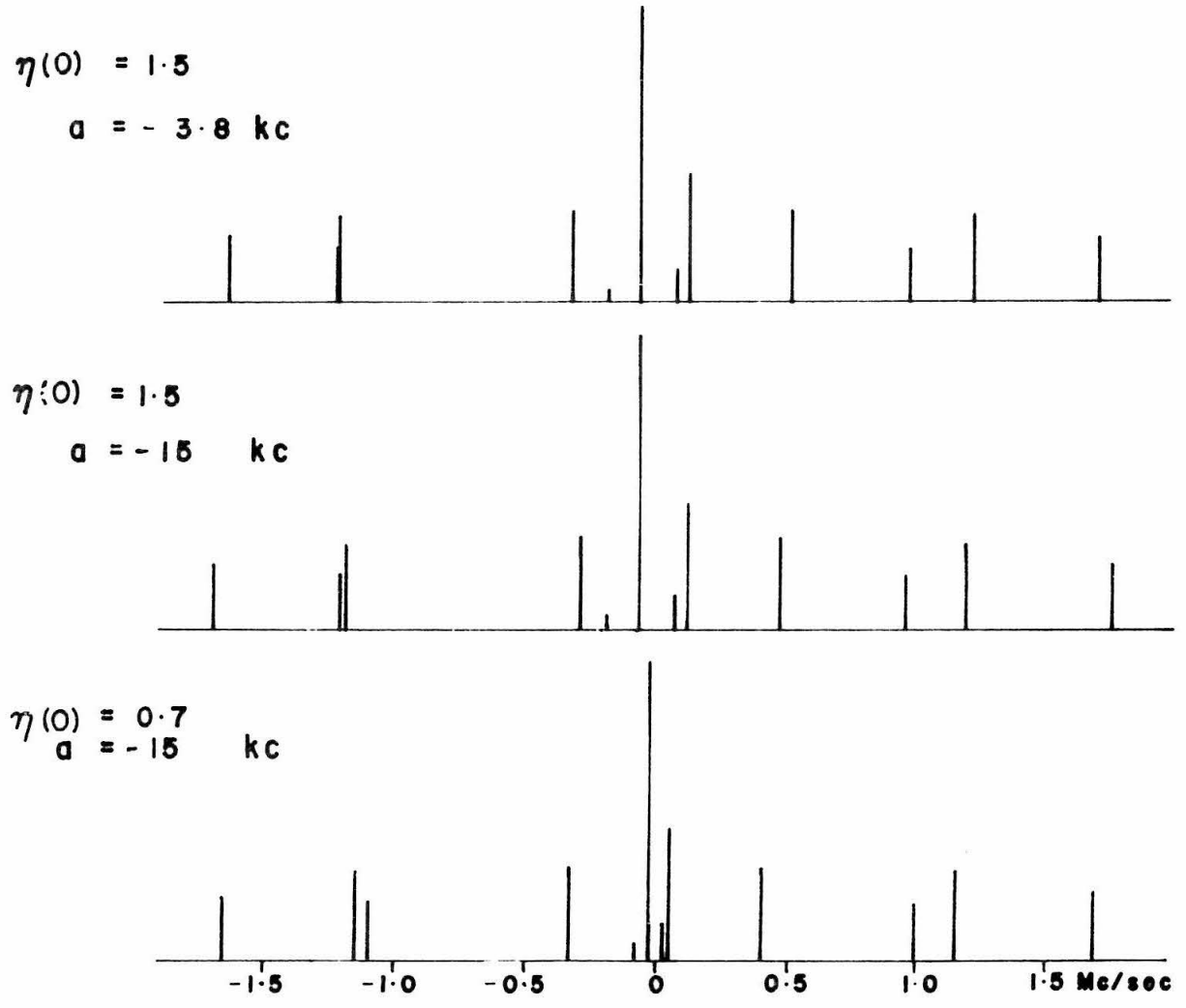
[a] All values are in a.u. The dipole moment has been computed using the oxygen nucleus as coordinate origin. All higher moments are referred to the center of mass of $H_2{}^{16}O$ as origin.

microwave hyperfine transition frequencies which form the basis for the experimental quadrupole coupling data cited in this work[29] are quite insensitive to the value of $\eta(O)$ between 0.7 and 1.5. Table XI gives the transition frequencies calculated with various values of $\eta(O)$ and a, the effective spin rotational constant of Stevenson and Townes.[29] The corresponding spectra are plotted in Figure 4 on the same relative scale. We thus find that the shifts in the transition frequencies of the hyperfine components upon increasing $\eta(O)$ from 0.7 to 1.5 are of the same order of magnitude as the shifts due to ^{17}O spin-rotation interaction. Since the observed spectrum is not well resolved, it is probable that it is not possible to distinguish between these two values of $\eta(O)$. Furthermore, in Stevenson and Townes' work, the dependence of the effective spin-rotational constant upon rotational state was ignored in approximating the spin-rotation interaction as $a\vec{I}\cdot\vec{J}$. In the appendix, we show that ignoring this dependence in going from the 2_{21} to the 2_{20} rotational states is equivalent to assuming that the rotational magnetic field per unit rotational angular momentum is almost identical at the oxygen nucleus for rotations about the b and c inertial axes (Figure 3). This assumption may or may not be an accurate one. We therefore believe that a comparison between the theoretical and experimental values of $\eta(O)$ is not particularly meaningful at the present stage.

Table XI. The $2_{20} \leftarrow 2_{21}$ microwave hyperfine transition frequencies of HDO^{17} calculated with various values of $\eta(O)$ and a, the effective spin rotational constant of Stevenson and Townes. $\vec{F} = \vec{I} + \vec{J}$ and 1 and 2 indicate initial and final hyperfine levels. Relative intensities are also given.

$F_2 \leftarrow F_1$	Relative intensities normalized to 100	Frequencies in Mc/sec relative to the unsplit line		
		$\eta(O) = 0.7$ a = -15 kc/sec	$\eta(O) = 1.5$ a = -15 kc/sec	$\eta(O) = 1.5$ a = -3.8 kc/sec
$\frac{9}{2} \leftarrow \frac{7}{2}$	6.17	-1.664	-1.703	-1.652
$\frac{3}{2} \leftarrow \frac{5}{2}$	8.00	-1.152	-1.191	-1.219
$\frac{1}{2} \leftarrow \frac{3}{2}$	5.19	-1.101	-1.211	-1.228
$\frac{5}{2} \leftarrow \frac{7}{2}$	8.57	-0.326	-0.287	-0.326
$\frac{1}{2} \leftarrow \frac{1}{2}$	1.48	-0.079	-0.189	-0.189
$\frac{3}{2} \leftarrow \frac{3}{2}$	27.35	-0.028	-0.067	-0.967
$\frac{9}{2} \leftarrow \frac{9}{2}$				
$\frac{5}{2} \leftarrow \frac{5}{2}$	3.43	0.028	0.067	0.067
$\frac{7}{2} \leftarrow \frac{7}{2}$	11.9	0.048	0.115	0.115
$\frac{7}{2} \leftarrow \frac{5}{2}$	8.57	0.402	0.469	0.508
$\frac{3}{2} \leftarrow \frac{1}{2}$	5.19	0.995	0.955	0.972
$\frac{5}{2} \leftarrow \frac{3}{2}$	8.00	1.152	1.191	1.219
$\frac{7}{2} \leftarrow \frac{9}{2}$	6.17	1.683	1.750	1.699

Figure 4. Hyperfine structure of the $2_{20} \leftarrow 2_{21}$ microwave transition of HDO^{17} calculated with various values of $\eta(O)$ and a, the effective spin rotational constant of Stevenson and Townes. All three spectra are plotted on the same relative scale, the unsplit line position (found experimentally at 10374.56 Mc/sec in Ref. 29) being taken as zero.


η(0) = 1·5
a = - 3·8 kc
η(0) = 1·5
a = - 15 kc
η(0) = 0·7
a = - 15 kc
-1·5
-1·0
-0·5
0
0·5
1·0
1·5 Mc/sec

4.4.2.2. Deuteron field gradient

The previous calculation of deuteron quadrupole coupling constants by Bersohn[84] used Ellison and Shull's wavefunction, which as mentioned earlier was obtained using inaccurate integrals. In contrast to the earlier effort of Bersohn, our present calculated deuteron quadrupole coupling constants are in good agreement with the experimental values. We recall that in our earlier work on formaldehyde,[66] the calculated values for these interaction constants differ from the experimental values by a factor of 1.7.

4.4.2.3 Hellmann-Feynman forces

The sum of the net forces on all nuclei for any molecular geometry should be zero for an approximate wavefunction in the Hartree-Fock limit, as has been shown by Kern and Karplus.[85] For an exact wavefunction, the net force on each nucleus in a molecule at the equilibrium geometry should be zero. The forces at the deuteron in water calculated with wavefunctions III and IV are very close to the true values but those at the oxygen nucleus are about as close as can be expected.[86]

4.4.2.4 Diamagnetic shieldings

An experimental value for the diamagnetic shielding at the oxygen nucleus in water is not available for comparison with our calculated value. However, if the electrostatic potential at the oxygen nucleus can be assumed to be independent of chemical bonding, then the diamagnetic shielding at the oxygen nucleus in water can be estimated from the Lamb term in atomic oxygen using the following

expression:[87]

$$\sigma^{d}_{H_2O}(O) \simeq \sigma^{d}_{atom}(O) + \frac{e^2}{3mc^2} \sum_{N' \neq O} \frac{Z_{N'}}{R_{ON'}}$$

σ^d for the oxygen atom has been calculated by Dickinson.[88] Using this value and the equilibrium geometry of the water molecule, a value of 414.6 ppm can be obtained, in excellent agreement with our calculated value. Finally, we note that both $\sigma^d(O)$ and $\sigma^d(H)$ are not particularly sensitive to the wavefunction.

4.4.2.5 Dipole, quadrupole, and octopole moments

All four of our wavefunctions as well as Neumann and Moskowitz's yielded dipole moments which are all slightly larger in magnitude than the experimental value. A limited configuration interaction with our minimal-basis-set wavefunction I,[89] however, was found to decrease the calculated dipole moment from 1.921 Debyes to 1.887 Debyes, bringing it closer to the experimental value. These results are in accord with Mulliken's views.[43] Presumably, configuration interaction would also improve the agreement between theory and experiment in the case of the other wavefunctions. We note that the dipole moments calculated for the first- and second-row diatomic hydrides using Hartree-Fock-limit wavefunctions have also been found to be slightly larger in magnitude than the experimental values.[90]

A recent review on molecular multipole moments lists previous theoretical values for the quadrupole and octopole moments of water.[91]

These values do not agree with our results, no doubt in part due to errors in the wavefunctions employed in these earlier works. On the other hand, our results for all components of the tensors agree quite closely with those of Neumann and Moskowitz both in sign and in magnitude. The same can be said of all the other one-electron properties calculated. This is remarkable in view of the large amount of computations involved and the somewhat artificial nature of gaussian basis functions.

5. Electronic structure

5.1 Contour maps

The electronic charge distribution in the water molecule predicted with our most elaborate wavefunction, wavefunction IX, has been plotted out pictorially in the form of contour maps. Figure 5 shows the map in the molecular plane and Figure 6 depicts that in the perpendicular plane bisecting the bond angle. The maps were generated by a computer program originally written in Fortran II by W. E. Palke and subsequently modified and adapted to the Fortran IV language by T. H. Dunning. The actual output generated by the program is a mesh of grid points at each of which a symbol representing the approximate electron density at that point is printed out. Contour lines of constant electronic density are then drawn manually by connecting lines through identical symbols. The maps therefore do not give accurate quantitative information about the charge distribution. They provide, however, a direct qualitative visualization of the charge distribution.

5.2. Nature of the chemical bond

As indicated by Stevenson and Townes, the asymmetry parameter of the field gradient at the oxygen nucleus in the water molecule can be related directly to the amount of s hybridization of the oxygen valence bonding orbitals by means of the Townes-Dailey theory. Since neither this relation nor the detailed steps leading to its derivation were given by Stevenson and Townes, we shall present the

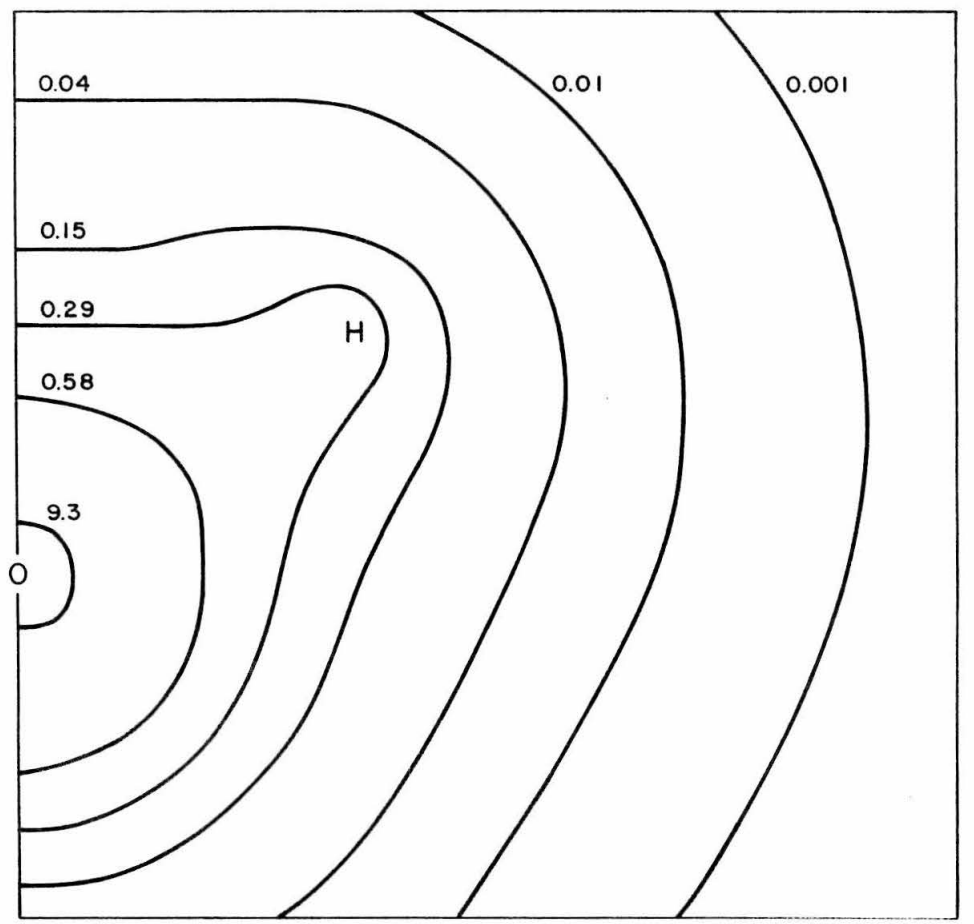


Figure 5. Contour map of the electron density (in a. u.) in the plane of the water molecule. Only a half-plane is shown.

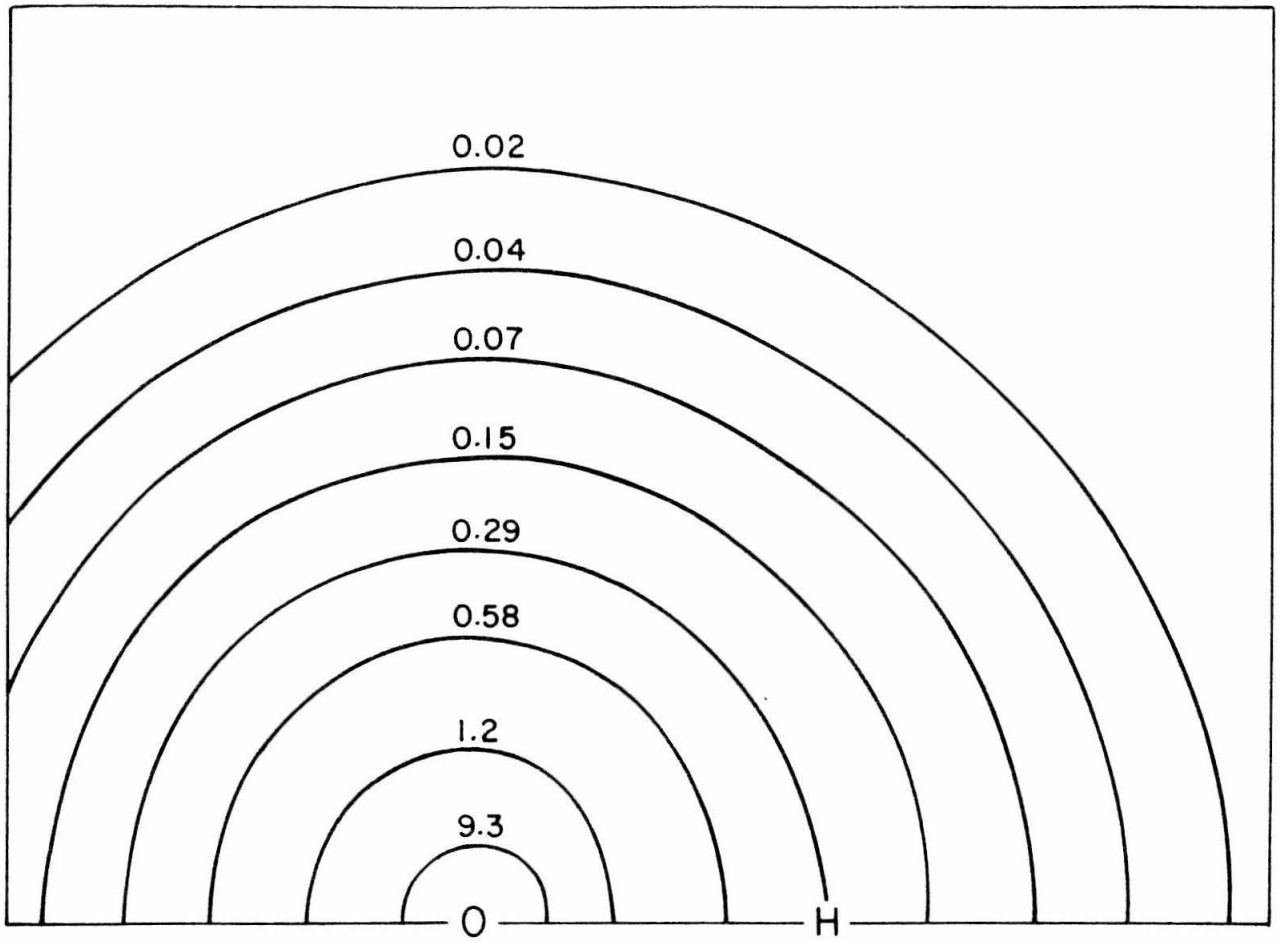


Figure 6. Contour map of the electron density (in a.u.) in the mirror plane bisecting the $H\hat{O}H$ angle. In this view, the two hydrogen nuclei coincide.

derivation here and subsequently deduce the percentage s hybridization of the oxygen bonding orbital in water corresponding to our calculated value of the field gradient asymmetry parameter at the oxygen nucleus.

Consider first an atom with a closed outer shell containing two 2s electrons and six 2p electrons. If q_{p_x}, q_{p_y}, and q_{p_z} are the contributions to the electric field gradient at the nucleus along any direction by each electron in the 2_{p_x}, 2_{p_y}, and 2_{p_z} orbitals, respectively, then the net field gradient in this direction is

$$2\,(q_{p_x} + q_{p_y} + q_{p_z}) = 0$$

on account of the closed-shell charge distribution. For the field gradient along the z direction, we have

$$q_{p_x} = q_{p_y}$$

and therefore $q_{p_x} = q_{p_y} = -\frac{1}{2}\, q_{p_z}$.

Thus for a non-closed shell atom or for a bonded atom, the net field gradient in the direction z is given by

$$q_{zz} = \left(-\frac{N_x + N_y}{2} + N_z \right) q_{210}$$

where N_x, N_y, and N_z are the effective number of electrons in the $2p_x$, $2p_y$, and $2p_z$ orbitals respectively, and q_{210} is the zz component of the field gradient tensor in the hydrogen atom with quantum numbers n = 2, ℓ = 1, and m = 0. The quantity

$$U_{pz} = \frac{N_x + N_y}{2} - N_z$$

is called the number of unbalanced p electrons along the z direction according to Townes and Dailey.[40] Thus

$$q_{zz} = -U_{pz}\, q_{210}$$

with similar expressions for q_{xx} and q_{yy}.

The oxygen valence orbitals in the water molecule are as follows:

$$\psi_1 = \sqrt{\alpha}\,|2s\rangle + (\tfrac{1}{2} - \alpha)^{1/2}\,|2p_z\rangle + \sqrt{\tfrac{1}{2}}\,|2p_x\rangle$$

$$\psi_2 = \sqrt{\alpha}\,|2s\rangle + (\tfrac{1}{2} - \alpha)^{1/2}\,|2p_z\rangle - \sqrt{\tfrac{1}{2}}\,|2p_x\rangle$$

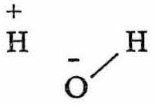
$$\psi_3 = \sqrt{\tfrac{1}{2} - \alpha}\,|2s\rangle - \sqrt{\alpha}\,|2p_z\rangle + \sqrt{\tfrac{1}{2}}\,|2p_y\rangle$$

$$\psi_4 = \sqrt{\tfrac{1}{2} - \alpha}\,|2s\rangle - \sqrt{\alpha}\,|2p_z\rangle - \sqrt{\tfrac{1}{2}}\,|2p_y\rangle$$

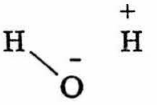
where the axes point in the directions shown in Figure 6.

The first two orbitals are bonding while the last two are non-bonding. The quantity α is the amount of s hybridization of the bonding orbitals.

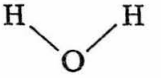
The following are the important valence bond structures for the water molecule:



I(i)



II(i)



III(1-2i)

The fractional importance of each structure is given in parentheses wherein i is called the ionic character of the bonds.

In calculating the field gradient at the oxygen nucleus, the contribution of each structure to N_x, N_y, and N_z is found to be as follows:

	I	II	III
N_z	$\left(\frac{3}{2}+\alpha\right)\frac{i}{1+\epsilon}$	$\left(\frac{3}{2}+\alpha\right)\frac{i}{1+\epsilon}$	$(1+2\alpha)(1-2i)$
N_x	$\frac{3}{2}\cdot\frac{i}{1+\epsilon}$	$\frac{3}{2}\cdot\frac{i}{1+\epsilon}$	$(1-2i)$
N_y	$2\cdot\frac{i}{1+\epsilon}$	$2\cdot\frac{i}{1+\epsilon}$	$2(1-2i)$

The factor of $\frac{1}{1+\epsilon}$ is that by which the field gradient of the oxygen atom is decreased due to negative ionization.

After a coordinate transformation, we thus find that the Townes-Dailey theory gives the following expressions for the field gradient components at the oxygen nucleus in the water molecule:

$$q_{aa} = (0.5 + 0.6008\ \alpha)\left(\frac{i}{1+\epsilon} + 1 - 2i\right)(-q_{210})$$

$$q_{bb} = (0.5 - 1.6007\ \alpha)\left(\frac{i}{1+\epsilon} + 1 - 2i\right)(-q_{210})$$

$$q_{cc} = (\alpha - 1)\left(\frac{i}{1+\epsilon} + 1 - 2i\right)(-q_{210})$$

where a, b, and c are the principal inertial axes of $HD^{17}O$ as shown in Figure 3. The field gradient asymmetry parameter

$$\eta(O) = \frac{q_{bb} - q_{cc}}{q_{aa}}$$

$$= \frac{1.5 - 2.6007\ \alpha}{0.5 + 0.6008\ \alpha}$$

is thus a function of α only, all terms in i and ϵ cancelling away. On solving the simple algebraic equation, we find that $\alpha = 0.38$ for $\eta(O) = 0.7$ (the experimental value of Stevenson and Townes) and that $\alpha = 0.21$ for $\eta(O) = 1.5$ (the value obtained in this thesis by ab initio calculation; see section 4.4.2.1).

Thus, the amount of s hybridization of the oxygen bonding orbital in the water molecule corresponding to our calculated value of the field gradient asymmetry parameter at the oxygen nucleus is 21%. This value lies between the values of 0% for pure p-bonds [92] and 25% for sp^3 tetrahedral bonds, [93] but is closer to the latter. The 38%

s hybridization indicated by the experimental value of $\eta(O)$ is less reasonable.

We note in passing that, through the percentage ionic character and hybridization of chemical bonds that it predicts in terms of the molecular electric field gradient, the Townes-Dailey theory provides a link between valence bond theory and any other theory of electronic wavefunctions with which one-electron properties can be calculated.

6. Conclusion

This thesis research shows that molecular Hartree-Fock theory can predict quite accurate one-electron properties provided the basis set is sufficiently large and judiciously chosen. The results which have been obtained are indeed encouraging and suggest several paths of further inquiry.

As pointed out at length in section 4.4.2.1, a discrepancy exists between present calculated and experimental values of the asymmetry parameter of the field gradient at the oxygen nucleus in the water molecule. At stake is not merely a resolution of this discrepancy but also an understanding of the nature of the chemical bond in the ground electronic state of the water molecule. As discussed in section 5.2, the present experimental value of the asymmetry parameter of the field gradient at the oxygen nucleus corresponds to an unusually high percentage of s hybridization in the oxygen bonding orbital according to the Townes-Dailey theory. The findings in this thesis indicate otherwise and suggest that it would be interesting to observe the $2_{20} \leftarrow 2_{21}$ rotational transition of $HD^{17}O$ at a resolution of about 20 kc/sec and subsequently analyse the high resolution microwave spectrum taking into account the dependence of the ^{17}O effective spin-rotation interaction constant upon rotational state.

There is a considerable amount of experimental data on the energy levels of excited electronic states of the water molecule.[38,39] Only a few of these Rydberg states have been characterized, however.

Recently, an electron impact excitation spectrum of the water molecule was reported by Compton et al.[94] A broad peak below the first excited singlet state of the water molecule was found, confirming somewhat less certain results reported earlier by Schulz.[95] The possibility that the observed peak could be due to the first triplet state of the water molecule has been raised. The possible existence of a stable triplet state below the first excited singlet state in the water molecule is of importance in understanding the radiation chemistry of water.[96] A theoretical calculation of the excited states of the water molecule would therefore clearly be of interest. As a first approximation, the excitation of the Rydberg electron may be assumed as not affecting the remaining electrons which may thus be described by Hartree-Fock molecular orbitals taken from the unperturbed molecular electronic wavefunction. The problem then reduces to the solution of the variational equation for the Rydberg orbital. Such a solution has recently been attempted by Lin and Duncan as mentioned in section 1.1. However, it is important to avoid the additional approximations made in their calculations. Thereby the assignment and nature of the Rydberg states of water may be clarified.[97]

The electronic wavefunctions reported in this thesis for the ground electronic state of the water molecule would also be suitable for perturbational calculations of molecular properties that depend on excited electronic states, in particular the nuclear spin-spin isotropic coupling constants, the paramagnetic susceptibility, and the electric polarizability.

Calculation of the Fermi-contact part of the nuclear spin-spin isotropic coupling constants in the water molecule can be readily attempted via the method of Pople and Santry [98] using the molecular orbitals calculated in this research. The H-D coupling in water was previously calculated by Pople and Santry using Ellison and Shull's inaccurate wavefunction, and a calculated value agreeing poorly with experiment was found. The paramagnetic susceptibility as well as the electric polarizability of the water molecule can be calculated according to the perturbed Hartree-Fock theory of Stevens, Pitzer, and Lipscomb.[99] Thereby our present understanding of these molecular properties may be evaluated.

In addition to the possibly fruitful investigations of the isolated water molecule mentioned above, we shall also point out several worthwhile paths of inquiry in connection with the intermolecular interactions of water.

First, the calculation of the third virial coefficient of steam should be attempted taking dipole-quadrupole interaction into account. The theoretical values of the molecular quadrupole moment components of water would have to be used, in view of the lack of a suitable method of direct measurement of the quadrupole moments of dipolar molecules. The dipole-quadrupole interaction may possibly resolve the existing discrepancy between calculated and experimental values for the third virial coefficient, as discussed in section 4.1.[100] In contrast, it has recently been concluded that the pressure broadening of the 1.64 mm rotational transition line of water vapour is

satisfactorily explained by dipole-dipole interaction alone.[101] It would be worthwhile to verify by actual calculation that the dipole-quadrupole contribution to the rotational linewidth is indeed negligible according to present theories of rotational linewidths. Thus a comparison may be made of the apparently differing dependence of the third virial coefficient and the rotational linewidth of water vapour on the intermolecular potential function.

Finally, the nature of the hydrogen bond in water merits investigation since hydrogen bonding is responsible for the unusual bulk properties of ice and liquid water.

The energies of hydrogen bonds lie intermediate between chemical bond energies and van der Waals interaction energies.[102] It thus appears that hydrogen bonds are not purely electrostatic in nature. This is supported by Morokuma and Pedersen's very recent theoretical study[103] of the water dimer via approximate Hartree-Fock wavefunctions for the entire 20-electron system. These investigators employed a medium-sized set of gaussian basis functions. Mulliken population analyses of the wavefunctions for several intermolecular configurations were interpreted to give the conclusion that hydrogen bond formation involves a delocalized transfer of electronic charge from proton acceptor to proton donor molecules. However, Morokuma and Pedersen found that the hydrogen bond strength, calculated as the difference between self-consistent-field energies of isolated and hydrogen-bonded molecules, was more than twice as large as experimental values. This appears somewhat surprising in

view of the fact that the same basis set was used in describing each water molecule in bonded and non-bonded form.

It is suggested that some alternative approach to the study of dimeric water should be sought. This is motivated by the prohibitive amount of computer time necessary for a complete SCF calculation of the dimeric system and by the encouraging findings of this thesis on the isolated molecule. As a preliminary step, the energy of one water molecule in the multipole field of another should be calculated. This energy consists of essentially two parts: the electrostatic energy arising from the static electronic charge distribution in the first molecule and that arising from its polarizability via the induction effect. The calculation can be done using the calculated polarizability tensor of the water molecule.[7] The outcome of such a calculation would be information on the fraction of the total stabilization energy of the hydrogen bond which can be accounted for by multipole interaction alone.

The complete intermolecular potential function for dimeric water includes, in addition to the above contributions from electrostatic and induction forces, three further contributions. These arise from the long-ranged dispersion forces, the intermediate-range second-order exchange forces, and the short-ranged valence forces. These forces have been calculated for simple atomic and molecular systems[104] but calculations of comparable accuracy have not been made on molecules as large as the water molecule.[105] Clearly, development of a tractable approximate theory of intermolecular

forces would be a logical second step to pursue in elucidating the nature of the hydrogen bond. The theory can be directly tested through calculation of the van der Waals constant $C_{H_2O-H_2O}$ for water vapour since a recent molecular beam scattering experiment [106] has yielded an experimental value for this constant.

Note added in proof (November 15, 1968): The $2_{20} \rightarrow 2_{21}$ rotational transition of $HD^{17}O$ has been observed under high resolution by Verhoeven, Dymanus, and Bluyssen (to be published). For the value of $\eta(O)$ as defined in this thesis, their best fit results give $\eta(O) = 1.583$ in good agreement with the ab initio calculations reported herein and elsewhere [Aung, Pitzer, and Chan, J. Chem. Phys. 49, 2071 (1968)]. Thus an existing discrepancy between theory and experiment has been resolved.

Appendix. Implication of Stevenson and Townes' Approximation concerning the ^{17}O Effective Spin Rotational Constant in $HD^{17}O$

The spin-rotational interaction Hamiltonian is

$$\mathcal{H}_{SR} = -\vec{I} \cdot \underset{\sim}{C} \cdot \vec{J}$$

where $\underset{\sim}{C}$ is the spin rotational interaction tensor. This Hamiltonian has been discussed by Chan and Dubin[107] and we shall follow their discussion in some detail.

If $\vec{F} = \vec{I} + \vec{J}$ and rotational states of an asymmetric rotor are labelled by $J\tau$,[60] then the first order spin-rotational interaction energy is

$$W_{SR} = -\sum_{g,g'} C_{gg'} \langle FIJ\tau | I_g J_{g'} | FIJ\tau \rangle$$

$$= -\sum_{g,g'} C_{gg'} \sum_{\tau'} \langle FIJ\tau | I_g | FIJ\tau' \rangle \langle FIJ\tau' | J_{g'} | FIJ\tau \rangle$$

$$= -\sum_{g,g'} C_{gg'} \sum_{\tau'} \frac{\langle FIJ\tau | J_g | FIJ\tau' \rangle \langle FIJ | \vec{J} \cdot \vec{I} | FIJ \rangle}{J(J+1)\hbar^2} \times \langle FIJ\tau' | J_{g'} | FIJ\tau \rangle$$

$$= -\sum_{g,g'} C_{gg'} \frac{\langle FIJ\tau | J_g J_{g'} | FIJ\tau \rangle}{J(J+1)\hbar^2} \langle FIJ | \vec{J} \cdot \vec{I} | FIJ \rangle$$

$$= -\sum_{g} C_{gg} \frac{\langle J\tau | J_g^2 | J\tau \rangle}{J(J+1)\hbar^2} \langle FIJ | \vec{I} \cdot \vec{J} | FIJ \rangle \qquad (A\text{-}1)$$

The third equality holds by virtue of an identity proved in Condon and Shortley.[108] (The identity is far more easily proved using the Wigner-Eckart Theorem,[109] however.)

The last equality follows from elementary group theoretical arguments. The asymmetric rotor belongs to the D_2 or V group.[62] The product of an asymmetric rotor wavefunction and its complex conjugate belongs to the totally symmetric representation of the above group. The operator $J_g J_{g'}$, however, transforms as a different irreducible representation unless $g = g'$. Thus the matrix element $\langle J\tau | J_g J_{g'} | J\tau \rangle$ vanishes for $g \neq g'$.

From equation (A-1), we can write

$$\mathcal{H}_{SR} = a\vec{I} \cdot \vec{J}$$

where the effective spin rotational constant is given by[107]

$$a = -\sum_g C_{gg} \frac{\langle J\tau | J_g^2 | J\tau \rangle}{J(J+1)\hbar^2}$$

It is therefore a function of the rotational state and will henceforth be so indicated, using the more modern notation $J_{K_{-1}K_1}$ in place of $J\tau$ for rotational state.[60]

We wish to investigate the implications of the assumption $a(2_{20}) = a(2_{21})$ for spin-rotation interaction in HDO^{17}.

The matrix element $\langle J_{K_{-1}K_1} | J_g^2 | J_{K_{-1}K_1} \rangle$ may be evaluated by expanding the asymmetric rotor wavefunction in terms of prolate

symmetric top wavefunctions $\psi_{J,K}$ in which representation the matrix elements of J_g^2 are easily evaluated:

$$|J_{K_{-1}K_1}\rangle = \sum_n a_{J,K_{-1}+2n}\,\psi_{J,K_{-1}+2n}$$

The summation is over all integral n values such that $|K_{-1}+2n| \leq J$.[60] The determination of the expansion coefficients $a_{J,K_{-1}+2n}$ and the subsequent evaluation of $\langle J_{K_{-1}K_1}|J_g^2|J_{K_{-1}K_1}\rangle$ are effected in practice by first setting up the rotational Hamiltonian matrix of $HD^{17}O$ and the J_g^2 matrix in the prolate symmetric top representation. For $J = 2$ and $K_{-1} = 2$, these matrices are of dimension 3×3. The transformation which diagonalizes the Hamiltonian matrix is then determined and applied to the J_g^2 matrix to give the matrix of J_g^2 in the representation of asymmetric top wavefunctions. The following results are found (in units of $\hbar^2$):

$$\langle 2_{20}|J_a^2|2_{20}\rangle = 3.9785, \quad \langle 2_{21}|J_a^2|2_{21}\rangle = 4$$

$$\langle 2_{20}|J_b^2|2_{20}\rangle = 1.2642, \quad \langle 2_{21}|J_b^2|2_{21}\rangle = 1$$

$$\langle 2_{20}|J_c^2|2_{20}\rangle = 0.7573, \quad \langle 2_{21}|J_c^2|2_{21}\rangle = 1$$

Therefore, the approximation

$$a(2_{20}) = a(2_{21})$$

implies that

$$(3.9785\ C_{aa} + 1.2642\ C_{bb} + 0.7573\ C_{cc})\frac{1}{6}$$

$$= (\quad 4\ C_{aa} + \quad C_{bb} + \quad C_{cc})\frac{1}{6}$$

or

$$\frac{C_{cc}}{C_{bb}} \simeq 1.09$$

From the physical meaning of the spin rotational interaction tensor, this in turn implies that the rotational magnetic field at the nucleus in question per unit rotational angular momentum is very nearly the same for rotations about the b and c inertial axes of $HD^{17}O$ (Figure 3).

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PART II

PERTURBATION-VARIATIONAL CALCULATION OF THE NUCLEAR SPIN-SPIN ISOTROPIC COUPLING CONSTANT IN HD

1. Introduction

1.1 Discovery of nuclear spin-spin isotropic coupling

The existence of fine structure in the nuclear magnetic resonance spectra of liquids was first reported by Proctor and Yu.[1] Subsequent investigators found the separations between multiplet components to be independent of temperature[2] and the strength of the external magnetic field.[2,3] From a consideration of these experimental findings, Gutowsky, McCall, and Slichter,[2] as well as Hahn and Maxwell[3] successfully deduced that the interaction responsible for the splittings is a coupling between neighbouring nuclei N and N′ of the form

$$J_{NN'}\ \vec{I}_N \cdot \vec{I}_{N'} \tag{1-1}$$

where $J_{NN'}$ is a coupling constant that is independent of the magnitude and direction of the applied magnetic field but is a function of the molecular electronic structure.

1.2 The origin of the coupling

An important mechanism for spin-spin isotropic coupling was first proposed by Ramsey and Purcell.[4] Using the HD molecule as an example, they suggested that the H and D nuclei can be coupled together via the electrons in the following qualitative manner: Each nuclear spin exerts an orienting influence on the electron spin of its atom via Fermi-contact interaction; the orienting influence is such as to align the electron spin anti-parallel to the spin of its nucleus.

The two electron spins, however, have a tendency to be aligned anti-parallel to each other. Thus there results a coupling between the two nuclei through the electrons, the effect of the coupling being a preferential alignment of the two nuclear spin directions relative to each other.

The general quantitative theory behind nuclear spin-spin coupling has subsequently been given by Ramsey [5] in terms of perturbation theory. From a consideration of the Hamiltonian for the interaction between the charges and magnetic moments of electrons with nuclear magnetic moments, Ramsey showed that the perturbational Hamiltonian giving rise to the spin-spin coupling consists of four terms:

$$\mathcal{H}' = \mathcal{H}_1^{(1)} + \mathcal{H}_1^{(2)} + \mathcal{H}_2 + \mathcal{H}_3 \tag{1-2}$$

where

$$\mathcal{H}_1^{(1)} = \sum_{k,\,N} 2\,\frac{1}{2m}\cdot\frac{|e|}{c}\cdot\frac{\hbar}{i}\cdot\hbar\,\gamma_N\left(\frac{\vec{I}_N\times\vec{r}_{kN}}{r_{kN}^3}\right)\cdot\vec{\nabla}_k$$

$$\mathcal{H}_1^{(2)} = \sum_{k,\,N,\,N'\neq N}\frac{1}{2m}\cdot\frac{e^2}{c^2}\cdot\gamma_N\hbar\cdot\gamma_{N'}\hbar\,\frac{\vec{I}_N\times\vec{r}_{kN}}{r_{kN}^3}\cdot\frac{\vec{I}_{N'}\times\vec{r}_{kN'}}{r_{kN'}^3}$$

$$\mathcal{H}_2 = g_S\beta\hbar\sum_{k,\,N}\gamma_N\left[\frac{3(\vec{S}_k\cdot\vec{r}_{kN})(\vec{I}_N\cdot\vec{r}_{kN})}{r_{kN}^5}-\frac{\vec{S}_k\cdot\vec{I}_N}{r_{kN}^3}\right]$$

$$\mathcal{H}_3 = \frac{8\pi}{3}\,g_S\,\beta\sum_{kN}\gamma_N\hbar\,\delta(\vec{r}_{kN})\,\vec{S}_k\cdot\vec{I}_N$$

m, e, g_S are the mass, charge and g-factor ($\simeq 2$) of the electron, γ_N is the gyromagnetic ratio of nucleus N and $\vec{I}_N$ its nuclear spin angular momentum in units of $\hbar$. $\vec{r}_{kN}$ is the position vector of the kth electron referred to nucleus N as origin. $\vec{S}_k$ is the electron spin angular momentum of electron k in units of $\hbar$ and β is the Bohr magneton. $\delta(\vec{r}_{kN})$ is the Dirac delta function defined such that its integral over all space containing nucleus N is unity:

$$\int \delta(\vec{r}_{kN})\, dv_k = 1$$

All remaining symbols have conventional meanings. $\mathcal{H}_3$ is the Hamiltonian for Fermi-contact interaction [5, 6, 7] between electronic and nuclear magnetic moments.

The nuclear-spin Hamiltonian for the electron-coupled interaction between nuclei N and N′ is obtained by collecting terms linear in each of the nuclear spins I_N and $I_{N'}$ from the expectation value of $\mathcal{H}'$ over electronic wavefunctions perturbed to first order in $\mathcal{H}'$. The isotropic coupling constant was thus found by Ramsey to consist of four contributions:

$$J_{NN'} = J^{(1)}_{1NN'} + J^{(2)}_{1NN'} + J_{2NN'} + J_{3NN'} \qquad (1\text{-}3)$$

where

$$J^{(1)}_{1NN'} = \frac{4}{3h}\gamma_N\gamma_{N'}\langle 0 \Big| \sum_k \frac{e^2\hbar^2}{2mc^2} \frac{\vec{r}_{kN}\cdot\vec{r}_{kN'}}{r^3_{kN}\, r^3_{kN'}} \Big| 0 \rangle$$

$$J^{(2)}_{1NN'} = -\frac{8}{3h}\hbar^2 \gamma_N \gamma_{N'} \sum_{nkj} \frac{1}{E_n - E_o} \langle 0 | \vec{m}^o_{kN} | n \rangle \cdot \langle n | \vec{m}^o_{jN'} | 0 \rangle ;$$

$$\vec{m}^o_{kN} = -\frac{1}{2m} \cdot \frac{|e|}{c} \cdot \frac{\hbar}{i} \left(\frac{\vec{r}_{kN}}{r^3_{kN}} \times \vec{\nabla}_k \right)$$

$$J_{2NN'} = -\frac{2}{3h} (g_S \beta \hbar)^2 \gamma_N \gamma_{N'} \sum_{nkj} \frac{1}{E_n - E_o} \langle 0 | \frac{3(\vec{S}_k \cdot \vec{r}_{kN})\vec{r}_{kN}}{r^5_{kN}} - \frac{\vec{S}_k}{r^3_{kN}} | n \rangle$$

$$\cdot \langle n | \frac{3(\vec{S}_j \cdot \vec{r}_{jN'})\vec{r}_{jN'}}{r^5_{jN'}} - \frac{\vec{S}_j}{r^3_{jN'}} | 0 \rangle$$

$$J_{3NN'} = -\frac{2}{3h} \left(\frac{8\pi}{3} \beta \hbar \, g_S \right)^2 \gamma_N \gamma_{N'} \sum_{nkj} \frac{1}{E_n - E_o} \langle 0 | \delta(\vec{r}_{kN}) \vec{S}_k | n \rangle$$

$$\cdot \langle n | \delta(\vec{r}_{jN'}) \vec{S}_j | 0 \rangle$$

For the HD molecule, Ramsey estimated that

$$J^{(1)}_{1HD} + J^{(2)}_{1HD} < 1 \text{ cps}$$

$$J_{2HD} \simeq 3 \text{ cps}$$

and

$$J_{3HD} \simeq 40 \text{ cps}$$

Since the experimental value is $J_{HD} = 43.0 \pm 0.5$ cps, [8] the dominant contribution to the coupling therefore appears to arise from Fermi-contact interaction. Subsequent independent calculations [9, 10] have

lent support to this conclusion.

1.3 Theoretical calculations of the coupling constant

There have been essentially three different ab initio approaches to the calculation of nuclear spin-spin isotropic coupling constants, namely the molecular orbital approach of McConnell,[11] the variational approach of Stephen,[9] and the valence bond approach made known by Karplus and Anderson.[12] Recently, a refinement of McConnell's molecular orbital approach has been developed by Pople and Santry.[13]

Both the McConnell and the Karplus-Anderson approaches are based on the perturbational formulas of Ramsey. Each infinite sum of integrals over excited state wavefunctions in Ramsey's formulas was replaced by a single term through the introduction of an "average" excitation energy ΔE:

$$\sum_{n \neq 0} \frac{\langle 0 | \mathcal{H}^i | n \rangle \langle n | \mathcal{H}^j | 0 \rangle}{W_n^o - W_o^o} \simeq \frac{1}{\Delta E} \left[\langle 0 | \mathcal{H}^i \mathcal{H}^j | 0 \rangle - \langle 0 | \mathcal{H}^i | 0 \rangle \langle 0 | \mathcal{H}^j | 0 \rangle \right] \tag{1-4}$$

McLachlan[14] has pointed out that it is dangerous to regard ΔE as an average excitation energy unless

$$\langle 0 | \mathcal{H}^i | n \rangle \langle n | \mathcal{H}^j | 0 \rangle$$

has the same sign for every excited state n. This means that the nature of the excited states must be carefully examined in each

application of the McConnell and the Karplus-Anderson approaches. The approaches thus lack general validity and at best require an uncertain estimate for the value of ΔE.

In the Pople-Santry refinement of McConnell's procedure, the average excitation energy approximation is avoided. Direct use is made of Ramsey's expressions for the various contributions to the coupling constant. The excited electronic states are assumed to arise from excitations of single electrons from an occupied molecular orbital ϕ_i into a virtual orbital ϕ_j, the excitation energy being taken as the difference in orbital energies, $\epsilon_j - \epsilon_i$.

Virtual orbitals are extraneous solutions to the Hartree-Fock equations. These extraneous solutions are obtained along with the ground-state molecular orbitals whenever the matrix Hartree-Fock equations of Roothaan[15] are solved and the number of basis functions used in the LCAO expansion exceeds the number of ground-state molecular orbitals. Since these extraneous molecular orbitals are eigenfunctions of the H-F operator defined in terms of ground-state molecular orbitals, they do not represent excited electronic states. For this reason, it appears that a justification of Pople and Santry's approximation of excited electronic states in terms of virtual orbitals will have to be based on an extensive comparison of the calculated nuclear spin-spin coupling constants with experimental measurements.

An approach to the calculation of nuclear spin-spin coupling constants which avoids the average excitation energy approximation and bypasses the need for knowledge of excited electronic state wavefunctions

is the variational approach developed by Stephen.[9] In this approach, Ramsey's perturbational formulas for the coupling constant are abandoned. The molecular electronic wavefunction is taken to be of the form

$$\psi = \psi_0 \left(1 + \sum_{\alpha} I_{N\alpha} f_{\alpha}^{(N)} + \sum_{\alpha} I_{N'\alpha} f_{\alpha}^{(N')} \right) \tag{1-5}$$

where ψ_0 is the unperturbed wavefunction, N and N′ denote the two coupled nuclei, α denotes a cartesian component of a vector, and $f_{\alpha}^{(N)}$, $f_{\alpha}^{(N')}$ are unknown functions or linear combinations of known functions with unknown coefficients to be determined. The expectation value of the perturbational Hamiltonian $\mathcal{H}'$, equation (1-2), is then taken and the energy term of the form

$$E_{NN'} = h J_{\alpha\beta} I_{N\alpha} I_{N'\beta}$$

is extracted, $J_{\alpha\beta}$ being thus a function of $f_{\alpha}^{(N)}$ and $f_{\alpha}^{(N')}$. By applying the variational principle to $E_{NN'}$, equations determining $f_{\alpha}^{(N)}$ and $f_{\alpha}^{(N')}$ result. The solution of these equations then enables a determination of the nuclear spin-spin coupling constant $J = \frac{1}{3} \sum_{\alpha} J_{\alpha\alpha}$ to be made.

In Stephen's calculation and a similar calculation by O'Reilly,[16] a delta function was included in the trial functions $f_{\alpha}^{(N)}$ in equation (1-5). The ambiguous results arising from the use of trial functions with delta-function singularities have been pointed out by Schaefer and Yaris.[17]

Ishiguro,[10] and also Das and Bersohn,[18] did not restrict the electronic wavefunction to be of the form (1-5) but instead employed a more general expansion for the wavefunction. They observed that the calculated coupling constant oscillated with the number of terms in the expansion although it never appeared to be far from the correct value.

Schaefer and Yaris[17] have critically discussed all the foregoing perturbation-variational calculations and performed an exploratory perturbation-variational calculation of the coupling constant in HD by including electron correlation in the electronic wavefunction. They found that the inclusion of electron correlation could improve the calculated coupling constant significantly. However, this conclusion appears to be only a tentative one since their best calculated value, obtained by including two electron-correlation terms in the wavefunction, is still very far from the experimental value.

1.4 Object of this thesis research

The calculation of nuclear spin-spin coupling constants is of importance because a comparison between calculated and experimental values for the constants provides an evaluation of our understanding and treatment of perturbed molecules. In cases where the coupling constants are previously unknown, approximate theoretical values can greatly facilitate the analyses of nuclear magnetic resonance spectra and can lead to the correlation of magnetic shielding and spin-spin coupling constants with electronic and molecular structures.[19]

In the preceding section, various theoretical approaches to the calculation of nuclear spin-spin coupling constants were summarized. The difficulties encountered in these approaches were discussed. Although encouraging results have been obtained in certain cases, there is evidently room for much improvement in theoretical development.

Recently a general perturbation-variational approach for calculating the Fermi-contact contribution to the nuclear spin-spin coupling constant in molecules has been developed by Professor R. M. Pitzer.[20] The approach avoids the average excitation energy approximation necessitated in the McConnell and the Karplus-Anderson approaches. The basis of the approach is molecular orbital theory; the Pople-Santry approximation of excited electronic states in terms of virtual orbitals is circumvented, however. The perturbational correction to the electronic wavefunction due to Fermi-contact interaction is described by using the proper functions, as has not been the case in the variational approach of Stephen and others. The form of the new kinds of basis functions is obtained from the exact first-order wavefunction of the hydrogen atom perturbed by Fermi-contact interaction. Although the approach requires the evaluation of a new kind of molecular integrals, these integrals have the same general forms for all molecular systems, so that initial efforts spent in developing the necessary computer programs will largely be non-recurrent and the calculation of coupling constants in molecules could become systematized. The approach thus attempts to achieve a level

of general applicability higher than possible in any of the existing approaches.

At its present stage of development, the theory behind the Pitzer approach lacks mathematical rigor owing to the assumption that electrons and nuclei are point particles. However, the intuitive arguments given where mathematical rigor cannot be given appear to be sound. A further point about the approach is that it does not take electron correlation into account. However, in the case of other electric and magnetic interactions due to one-electron perturbing Hamiltonians, Lipscomb and collaborators[21] have recently shown that electron correlation probably plays only a minor role insofar as these interactions could be calculated in good agreement with experiment without the inclusion of correlation corrections. The Pitzer approach assumes that such is also the case with the nuclear spin-spin coupling interaction, although this interaction involves a one-electron perturbing Hamiltonian which depends on electron spin. In any case, any question about the importance of electron correlation cannot be settled until calculated results obtained without using correlated wavefunctions are compared first with experimental measurements and then, if possible, with results calculated using correlated wavefunctions.

From the considerations given in the preceding paragraphs, it is clearly of interest to submit the perturbation-variational theory of R. M. Pitzer to a test. In this thesis research, therefore, the theory is applied to the calculation of the nuclear spin-spin coupling constant in the HD molecule. This molecule has been chosen for three reasons.

First, the sign as well as the magnitude of the coupling constant in the HD molecule has been determined experimentally [8] and a comparison of the calculated value with experiment is therefore possible. Secondly, the new kind of molecular integrals encountered make the HD molecule the simplest molecule to which the approach can be applied. Lastly, molecular orbital wavefunctions for its unperturbed electronic ground state are either already available in the literature [22] or can be computed to various degrees of accuracy. The immediate purpose of this thesis research, however, is to investigate the practicality of the new approach and we shall therefore employ only a minimal basis set description of the unperturbed molecule.

2. The perturbation-variational approach of R. M. Pitzer

In the next four sections, we give a brief discussion of R. M. Pitzer's perturbation-variational theory of nuclear spin-spin coupling constants. The material presented in section 2.2 and the first half of section 2.3 closely follows the contents of a set of Professor Pitzer's personal notes by permission. Full details of the theory will be found in a forthcoming publication.[20]

2.1 Basic idea

The Pitzer approach to the calculation of nuclear spin-spin coupling constants assumes that the only important contribution to the coupling arises from Fermi-contact interaction. Since the coupling we are interested in is an isotropic one, only a single term in the vector dot product of the Fermi-contact Hamiltonian need be taken and the perturbational Hamiltonian therefore takes the form

$$\mathcal{H}^1_A = \frac{8\pi}{3} g_S \beta \gamma_A \hbar^2 \sum_k \delta(\vec{r}_{kA}) S_{kz} I_{Az} \qquad (2\text{-}1)$$

where A denotes one of the two coupled nuclei and the subscript z denotes cartesian components of the spin vectors along an arbitrary direction of spin quantization. The remaining rotation follows that of section 1.2.

The Pitzer approach employs the molecular orbital description of molecules. The aim is to calculate the small amount by which the electron spin distribution in the unperturbed molecule is distorted by Fermi-contact interaction at one of the two coupled nuclei. The

distortion takes the form of a first-order perturbational correction for each molecular spinorbital. The form of the basis functions necessary to describe the first-order perturbational correction to each molecular orbital may be investigated by solving for the first-order correction to the wavefunction of the hydrogen atom due to the Fermi-contact interaction. To obtain the form of the first-order wavefunction, the perturbational Hamiltonian may be taken as

$$h^1 = \frac{\delta(r)}{r^2} \tag{2-2}$$

where the one-dimensional Dirac delta function is defined such that

$$\int_0^a \delta(r)\, dr = 1 , \qquad a > 0$$

The first order perturbational equation in atomic units for the ground-state hydrogen atom is thus

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} - E^0 \right) \psi^1 = -\left(\frac{\delta(r)}{r^2} - E^1 \right) \psi^0 \tag{2-3}$$

where

$$\psi^0 = \sqrt{\frac{Z^3}{\pi}}\, e^{-Zr}$$

$$E^0 = -\frac{1}{2} Z^2$$

$$E^1 = \langle \psi^0 | h^1 | \psi^0 \rangle = 4\, Z^3$$

and

Z = nuclear charge

The solution, first given by Schwartz[23] and derived in Appendix A, is

$$\psi^1 = 2\sqrt{\frac{Z^3}{\pi}}\left(-\frac{1}{r} + 2\,Z\,\ell n\,r + 2\,Z^2 r + C\right)e^{-Zr} \qquad (2\text{-}4)$$

where ℓn denotes the natural logarithm and C is a constant. The solution indicates that in addition to the usual Slater-type orbitals, two new types of basis functions are needed to describe the perturbational correction to the wavefunction. The new functions have the forms $\frac{e^{-r}}{r}$ and $e^{-r}\,\ell n\,r$. That orbitals of these types are necessary is also indicated by the cusp equations derived in section 2.4.

The form of the basis functions for the first-order molecular orbitals being thus specified, the Pitzer theory proceeds to derive equations for the first-order molecular orbital coefficients by means of the variational principle.

The energy of interaction between two nuclear magnetic moments in a molecule can be written in the form[18]

$$J_{AA}\gamma_A^2 + J_{AB}\gamma_A\gamma_B + J_{BB}\gamma_B^2 \qquad (2\text{-}5)$$

where γ_A and γ_B are the gyromagnetic ratios of the two nuclei A and B. In the Pitzer approach, the variational principle is applied to either one of the two self-coupling terms, say $J_{AA}\gamma_A^2$, under the appropriate constraints and assuming that the only important contribution to the coupling energy arises from Fermi-contact interaction. One factor of γ_A comes from the perturbational Hamiltonian (2-1); the other factor comes from the first-order correction to the

molecular spinorbitals due to this perturbation. The equations resulting from the application of the variational principle are solved for the first-order molecular orbital coefficients. The effect of this distortion in the wavefunction on the energy of Fermi-contact interaction at the other coupled nucleus B is then calculated and gives the desired internuclear spin-spin coupling. The final step in the calculation of the nuclear spin-spin coupling constant between nuclei A and B in a closed shell system of 2n electrons thus consists of extracting terms linear in each of the gyromagnetic ratios γ_A and γ_B from the expectation value

$$\sum_{m=1}^{2n} \langle \psi_m^0 + \psi_{mA}^1 | \mathcal{H}_B^1 | \psi_m^0 + \psi_{mA}^1 \rangle$$

where ψ_m^0 is an unperturbed molecular spinorbital and ψ_{mA}^1 the perturbational correction to ψ_m^0 due to $\mathcal{H}_A^1$ defined in (2-1). The result is

$$J_{AB} I_{AZ} I_{BZ} = \sum_{m=1}^{2n} \left[\langle \psi_m^0 | \mathcal{H}_B^1 | \psi_{mA}^1 \rangle + \langle \psi_{mA}^1 | \mathcal{H}_B^1 | \psi_m^0 \rangle \right] \qquad (2\text{-}6)$$

It is to be noted that in Stephen's variational approach, the internuclear coupling term $J_{AB}\gamma_A\gamma_B$ in (2-5) is made stationary. It has been pointed out in general by Das and Bersohn [18] that if the exact unperturbed wavefunction is used, then equivalent results for the coupling constant J_{AB} would be obtained by making any one of the three terms in (2-5) stationary and that if an approximate unperturbed

wavefunction is used, then there is no criterion for a preference.

2.2 The equations for the first-order molecular orbital coefficients

Consider a closed-shell system with 2n electrons. ψ and ϕ each with an appropriate index denote a molecular spinorbital (MSO) and a molecular orbital (MO) respectively. Pitzer used the following rotation for indices:

a, b	going from 1 to 2n over MSO's (1 ··· n for up spins, n+1 ··· 2n for down spins)
i, j, k	going from 1 to n over MO's
p, q	going from 1 to m_0 over basis functions
α, β, γ	going from 1 to m_1 over basis functions

The values $\alpha, \beta, \gamma = m_0 + 1,\ m_0 + 2 \cdots\cdots m_1$ refer to basis functions used exclusively in the expansion of the first-order molecular orbitals.

The nuclear spin factors are regarded as constants and, together with the numerical constants in the Fermi-contact Hamiltonian, may be suppressed until the very last stage of the calculation indicated by equation (2-6). Hence the one-electron perturbational Hamiltonian corresponding to (2-1) becomes

$$H^1 = 2 \frac{\delta(r)}{r^2} \cdot S_Z \qquad (2\text{-}7)$$

dropping the nuclear label from H^1 for convenience. The corresponding spin-free operator is

$$h^1 = \frac{\delta(r)}{r^2} \tag{2-8}$$

The following expansions from Hartree-Fock perturbation theory[24] are made:

$$\psi_a = \psi_a^0 + \psi_a^1 + \cdots\cdots$$

$$\phi_i = \phi_i^0 \pm \phi_i^1 + \cdots\cdots$$

$$\phi_i^0 = \sum_p C_{pi} \chi_p$$

$$\phi_i^1 = \sum_\alpha C_{\alpha i}^1 \chi_\alpha$$

$$h = h^0 + h^1 + \cdots\cdots \tag{2-9}$$

h^0 is the unperturbed Hamiltonian for an electron moving in the field of the bare nuclei. ψ_a^1 is assumed to have the same electron spin factor as ψ_a^0. That is, the perturbation to first order is assumed to affect only the spatial part of each MSO. From the form of H^1 in (2-7), the first-order correction to each molecular orbital is expected to be the same in magnitude but to differ in sign for up and down electron spins, hence the two signs in the expansion for ϕ_i in equations (2-9). To elaborate, if

$$\psi_a = \phi_i \alpha \tag{2-10}$$

and

$$\psi_{a+n} = \phi_i \beta$$

then to first order in the perturbation, we shall have

$$\psi_a = (\phi_i^0 + \phi_i^1)\,\alpha$$

$$\text{and} \qquad \psi_{a+n} = (\phi_i^0 - \phi_i^1)\,\beta \tag{2-11}$$

The starting point in the theory is the variational function

$$E' = \sum_a (\psi_a\, h\, \psi_a) + \frac{1}{2} \sum_{a,b} \left[(\psi_a \psi_a | \psi_b \psi_b) - (\psi_a \psi_b | \psi_a \psi_b) \right]$$

$$- \sum_{a,b} \epsilon_{ab} (\psi_a \psi_b) \tag{2-12}$$

which is to be an extremum to all orders in the perturbation. The electron labels in the integrand of the electron repulsion integrals $(\psi_a \psi_a | \psi_b \psi_b)$ and $(\psi_a \psi_b | \psi_a \psi_b)$ are in the usual sequence [see, for example, equation (4-14) of Thesis Part I]. The ϵ_{ab}'s are the usual Lagrange multipliers and have the following expansion in orders of the perturbation:

$$\epsilon_{ab} = \epsilon_{ab}^0\, \delta_{ab} + \epsilon_{ab}^1 + \cdots\cdots$$

where δ_{ab} is the Kronecka del.

The first order part of E' can be shown to vanish by virtue of ϕ_i^1 having opposite signs for up and down electron spins as indicated in (2-10) and (2-11).

A general principle of perturbation theory states that the second order energy can be obtained by using the wavefunction correct to

first order in the perturbation.[25] The second order part of (2-12) may be reduced to the following forms:

$$
\begin{aligned}
E'^{(2)} = & \sum_i \{ 8(\phi_i^1 h^1 \phi_i^0) + 2(\phi_i^1 h^0 \phi_i^1) \} + \tfrac{1}{2} \sum_{ij} \{ \delta(\phi_i^1 \phi_i^1 | \phi_j^0 \phi_j^0) \\
& - 4(\phi_i^1 \phi_j^1 | \phi_i^0 \phi_j^0) - 4(\phi_i^1 \phi_j^0 | \phi_i^1 \phi_j^0) - 4(\phi_i^1 \phi_j^0 | \phi_i^0 \phi_j^1) \} \\
& - \sum_i 2\epsilon_i^0 (\phi_i^1 \phi_i^1) - 2 \sum_{ij} (\epsilon_{ij}^1 + \epsilon_{ji}^1)(\phi_i^0 \phi_j^1) \\
= & \; 4 \sum_{\alpha i} C_{\alpha i}^1 h_{\alpha i}^1 + 2 \sum_{\alpha \beta i} C_{\alpha i}^1 h_{\alpha\beta}^0 C_{\beta i}^1 + 4 \sum_{\alpha\beta ij} C_{\alpha i}^1 C_{\beta i}^1 (\alpha\beta | jj) \\
& - 2 \sum_{\alpha\beta ij} C_{\alpha i}^1 C_{\beta j}^1 (\alpha\beta | ij) - 2 \sum_{\alpha\beta ij} C_{\alpha i}^1 C_{\beta i}^1 (\alpha j | \beta j) \\
& - 2 \sum_{\alpha\beta ij} C_{\alpha i}^1 C_{\beta j}^1 (\alpha j | i\beta) - 2 \sum_{\alpha\beta i} \epsilon_i^0 C_{\alpha i}^1 C_{\beta i}^1 S_{\alpha\beta} \\
& - 4 \sum_{\alpha ij} \epsilon_{ij}^{1\prime} C_{\alpha i}^1 S_{\alpha i} \qquad (2\text{-}13)
\end{aligned}
$$

where $S_{\alpha\beta} = (\chi_\alpha \chi_\beta)$

$S_{\alpha j} = (\chi_\alpha \phi_j^0)$

and $\epsilon_{ij}^{1\prime} = \dfrac{\epsilon_{ij} + \epsilon_{ji}}{2}$ is a symmetric matrix element. The prime will subsequently be dropped for convenience so that $\epsilon_{ij}^{1\prime}$ will henceforth be denoted simply as ϵ_{ij}^1.

$E'^{(2)}$ contains divergent integrals. These are listed in Table I where χ is any basis function which is finite and non-zero at $r = 0$,

Table I. Divergent integrals in the second order self coupling energy expression[a]

Integral	Diverging value
$\int \left(N_\alpha \frac{e^{-k_\alpha r}}{r} \right) \frac{\delta(r)}{r^2} \chi \, dV$	$\frac{1}{0} (r\chi_\alpha)_{r=0} (\chi)_{r=0} 4\pi$
$\int \left(N_\alpha e^{-k_\alpha r} \ln r \right) \frac{\delta(r)}{r^2} \chi \, dV$	$\ln 0 \left(\frac{\chi_\alpha}{\ln r} \right)_{r=0} (\chi)_{r=0} 4\pi$
$\int \left(N_\alpha \frac{e^{-k_\alpha r}}{r} \right) (-\frac{1}{2}\nabla^2) \left(N_\beta \frac{e^{-k_\beta r}}{r} \right) dV$	$\frac{1}{0} (r\chi_\alpha)_{r=0} (r\chi_\beta)_{r=0} 2\pi$
$\int \left(N_\alpha e^{-k_\alpha r} \ln r \right) (-\frac{1}{2}\nabla^2) \left(N_\beta \frac{e^{-k_\beta r}}{r} \right) dV$	$\ln 0 \left(\frac{\chi_\alpha}{\ln r} \right)_{r=0} (r\chi_\beta)_{r=0} 2\pi$
$\int \left(N_\alpha \frac{e^{-k_\alpha r}}{r} \right) (-\frac{Z}{r}) \left(N_\beta \frac{e^{-k_\beta r}}{r} \right) dV$	$\ln 0 (r\chi_\alpha)_{r=0} (r\chi_\beta)_{r=0} (-4\pi)(-Z)$

[a] χ is any basis function which is finite and non-zero at r = 0.

N_α and N_β being constant factors used in the definitions of the singular basis functions.

The expression (2-13) for $E'^{(2)}$ therefore consists of three groups of terms listed below in decreasing orders of magnitude:

(i) a group of terms having a common factor diverging as $\frac{1}{0}$.

(ii) a group of terms having a common factor diverging as $\ell n\, 0$.

(iii) a group of finite terms.

The first group of terms, save for the common divergent factor, is

$$E'^{(2)}_{\frac{1}{0}} = 16\pi \sum_i (\phi_i^0)_{r=0} \sum_\alpha C^1_{\alpha i} (r\chi_\alpha)_{r=0} + 4\pi \sum_i \left[\sum_\alpha C^1_{\alpha i} (r\chi_\alpha)_{r=0} \right]^2 \qquad (2\text{-}14)$$

Since by $\frac{1}{0}$ we mean 1 divided by an arbitrarily small number, the first group of terms are arbitrarily more important than the other terms and therefore any coefficients involved should be determined by minimizing the first group of terms by themselves. Thus we have

$$\frac{\partial E'^{(2)}_{\frac{1}{0}}}{\partial \sum_\alpha C^1_{\alpha j} (r\chi_\alpha)_{r=0}} = 16\pi (\phi_j^0)_{r=0} + 8\pi \sum_\alpha C^1_{\alpha j} (r\chi_\alpha)_{r=0} = 0$$

so that

$$\sum_\alpha C^1_{\alpha j} (r\chi_\alpha)_{r=0} = -2(\phi_j^0)_{r=0} \qquad (2\text{-}15)$$

This is Pitzer's first equation for the first-order molecular orbital coefficients. It gives in conjunction with (2-14)

$$E'^{(2)}_{\frac{1}{0}} = -16\pi \sum_i \left[(\phi_i^0)_{r=0} \right]^2 \qquad (2\text{-}16)$$

In the second group of terms of $E'^{(2)}$, the finite factor multiplying $\ell n\, 0$ is found to be uniquely determined by (2-15). Save for the common divergent factor, this group of terms is found to be

$$E'^{(2)}_{\ell n\, 0} = 32\pi Z \sum_i \left[(\phi_i^0)_{r=0} \right]^2 \qquad (2\text{-}17)$$

and therefore does not give any new condition on the first-order molecular orbital coefficients.

Finally the group of finite terms in $E'^{(2)}$ is to be an extremum under the constraint (2-15) for which a new set of Lagrange multipliers λ_i have to be introduced:

$$E''^{(2)} = E'^{(2)} - 4 \sum_{\alpha i} C^1_{\alpha i} (r\chi_\alpha)_{r=0} \lambda_i \qquad (2\text{-}18)$$

Differentiating (2-18) with respect to $C^1_{\gamma k}$ gives, after rearrangement of terms,

$$h^1_{\gamma k} - \sum_i S_{\gamma i} \epsilon^1_{ik} + \sum_\alpha (f^0_{\gamma\alpha} - \epsilon^0_k S_{\gamma\alpha}) C^1_{\alpha k}$$

$$- \sum_{\alpha i} C^1_{\alpha i} [(\gamma\alpha \,|\, ik) + (\gamma i \,|\, k\alpha)] - \lambda_k (r\chi_\gamma)_{r=0} = 0 \qquad (2\text{-}19)$$

where

$$f^0_{\gamma\alpha} = h^0_{\gamma\alpha} + \sum_i [2(\gamma\alpha|ii) - (\gamma i|\alpha i)] \qquad (2\text{-}20)$$

The freedom to a first-order unitary transformation of the molecular orbitals amounts only to the mixing of zero order molecular orbitals into first-order molecular orbitals with first-order coefficients. This transformation is used to diagonalize ϵ^1_{ik}, giving

$$h^1_{\gamma k} - \epsilon^1_k S_{\gamma k} + \sum_\alpha (f^0_{\gamma\alpha} - \epsilon^0_k S_{\gamma\alpha})\, C^1_{\alpha k}$$

$$- \sum_{\alpha i} C^1_{\alpha i} [(\gamma\alpha|ik) + (\gamma i|k\alpha)] - \lambda_k (r\,\chi_\gamma)_{r=0} = 0 \qquad (2\text{-}21)$$

This is Pitzer's second equation for the first-order molecular orbital coefficients. In this equation, all divergent terms must be excluded except that any finite part of a divergent integral must be retained.

From orthogonality and normalization requirements, we have

$$(\phi^0_j + \phi^1_j | \phi^0_k + \phi^1_k) = 0, \qquad j \neq k \qquad (2\text{-}22)$$

and

$$(\phi^0_k + \phi^1_k | \phi^0_k + \phi^1_k) = 1 \qquad (2\text{-}23)$$

Since the right-hand-side numbers are exact to all orders in the perturbation, we have

$$(\phi^0_j \phi^1_k) + (\phi^1_j \phi^0_k) = 0, \qquad j \neq k \qquad (2\text{-}24)$$

and $$(\phi_k^0 \phi_k^1) = 0 \qquad (2\text{-}25)$$

To see whether any of these conditions are already contained in (2-21), we note that (2-21) holds for any basis function χ_γ, be it a basis function used exclusively for the first-order molecular orbitals, or one originally present in the unperturbed molecular orbitals, say χ_p. In the latter case, multiplying by C_{pj}^0 and summing over p gives

$$h_{jk}^1 - \epsilon_k^1 \delta_{jk} + (\epsilon_j^0 - \epsilon_k^0) \sum_\alpha S_{j\alpha} C_{\alpha k}^1$$

$$- \sum_{\alpha i} C_{\alpha i}^1 [(j\alpha|ik) + (ji|k\alpha)] = 0 \qquad (2\text{-}26)$$

where j and k indicate matrix elements involving ϕ_j^0 and ϕ_k^0. For $j \neq k$, interchanging j and k gives (2-24) so that this orthogonality condition is contained in (2-21). For j = k, (2-26) gives

$$\epsilon_k^1 = h_{kk}^1 - 2 \sum_{\alpha i} C_{\alpha i}^1 (k\alpha|ik)$$

Thus, the normalization condition (2-25) is not contained in (2-21) and may be written as

$$\sum_\alpha S_{k\alpha} C_{\alpha k}^1 = 0 \qquad (2\text{-}27)$$

This is Pitzer's third and last equation for the first-order molecular orbital coefficients.

The three equations (2-15), (2-21), and (2-27) provide a set of $n(m_1 + 2)$ equations in the same number of unknowns $C^1_{\alpha k}$, ϵ^1_k, λ_k ($\alpha = 1 \cdots\cdots m_1$; $k = 1 \cdots\cdots n$).

2.3 Rationalization and treatment of divergent integrals

Pitzer considered the infinite quantities appearing as $\frac{1}{0}$ and $\ell n\, 0$ as being not infinite in reality but only very large in magnitude. Since nuclei and electrons are actually finite in size, the zeroes must actually be replaced by some parameter r_0 of the order of the classical electron radius r_e in atomic units. Now, r_e in atomic units is given by the fine-structure constant squared:

$$r_e = \alpha^2$$

while the numerical factor in the perturbational Hamiltonian H^1, equation (2-7), which has been suppressed in the development of the theory is

$$\frac{\frac{8\pi}{3}\gamma_N \hbar\, \gamma_S \hbar \cdot \frac{1}{a_0^3}}{\hbar^2/m a_0^2} = \frac{8\pi}{3} \cdot g_N g_S \left(\frac{e\hbar}{2mc} \cdot \frac{e\hbar}{2Mc} \right) \frac{1}{a_0^3} \cdot \frac{m a_0^2}{\hbar^2}$$

$$= \frac{8\pi}{3}\, g_N g_S \frac{e^4}{4\hbar^2 c^2} \cdot \frac{m}{M}$$

$$= \frac{2\pi}{3}\, g_N g_S \alpha^2 \cdot \frac{m}{M}$$

$$\simeq \frac{\alpha^2}{10^3}$$

where M is the proton mass and the remaining notations have conventional meanings. Therefore

$$E'^{(2)} \simeq \left(\frac{\alpha^2}{10^3}\right)^2 \cdot \frac{1}{r_e}$$

$$\simeq \frac{r_e^2}{10^6} \cdot \frac{1}{r_e}$$

$$\simeq \frac{r_e}{10^6}$$

so that $E'^{(2)}$ would in fact be finite.

We further rationalize that since the divergent factors have coefficients which do not depend on the first-order molecular orbitals, [see equations (2-16) and (2-17)] these divergent terms in the second-order energy expression may be considered as constants as far as variations in the first-order molecular orbital coefficients are concerned.

A list of the divergent integrals occurring in the Pitzer theory was given in section 2.2. As already noted, equation (2-21) was derived under the condition such that all divergent terms must be excluded from that equation except for those terms arising from the finite parts of divergent integrals.

In Table II, we give a list of divergent integrals which have finite parts for the general case where an arbitrary number of singular

Table II. Finite parts of divergent integrals [a]

	Divergent integral	Finite part
(1)	$\int_0^\infty \left(N_\alpha \frac{e^{-k_\alpha r}}{k_\alpha r} \right) \frac{\delta(r)}{r^2} \chi\, r^2\, dr$	$-N_\alpha (\chi)_{r=0}$
(2)	$\int_0^\infty [N_\alpha e^{-k_\alpha r} \ell n(2\gamma k_\alpha r)] \frac{\delta(r)}{r^2} \chi\, r^2\, dr$	$N_\alpha [\ell n (2 k_\alpha)] (\chi)_{r=0}$
(3)	$\int_0^\infty \left(N_\alpha \frac{e^{-k_\alpha r}}{k_\alpha r} \right) (-\tfrac{1}{2}\nabla^2) \left(N_\beta \frac{e^{-k_\beta r}}{k_\beta r} \right) r^2\, dr$	$-\frac{1}{2} \frac{N_\alpha N_\beta}{k_\alpha} \left(\frac{k_\beta}{k_\alpha + k_\beta} + \frac{k_\alpha}{k_\beta} \right)$
(4)	$\int_0^\infty \left(N_\beta \frac{e^{-k_\beta r}}{k_\beta r} \right) (-\tfrac{1}{2}\nabla^2) [N_\alpha e^{-k_\alpha r} \ell n(2\gamma k_\alpha r)] r^2\, dr$	$\frac{1}{2} N_\alpha N_\beta \left[\frac{k_\alpha (2k_\beta + k_\alpha)}{k_\beta (k_\beta + k_\alpha)^2} \left(1 + \ell n \frac{2k_\alpha}{k_\beta + k_\alpha} \right) - \frac{1}{k_\beta} + \frac{1}{k_\beta} \ell n (k_\beta + k_\alpha) \right]$
(5)	$\int_0^\infty \left(N_\alpha \frac{e^{-k_\alpha r}}{k_\alpha r} \right) (-\frac{Z}{r}) \left(N_\beta \frac{e^{-k_\beta r}}{k_\beta r} \right) r^2\, dr$	$Z N_\alpha N_\beta \frac{1}{k_\alpha k_\beta} \ell n (k_\alpha + k_\beta)$

[a] χ is any basis function which is finite at $r = 0$.

basis functions with different exponents are used in expanding the first-order molecular orbital. In this table, the singular basis functions have been defined as

$$N_{\alpha} \frac{e^{-k_{\alpha} r}}{k_{\alpha} r}$$

and $$N_{\beta} e^{-k_{\beta} r} \ln (2 \gamma k_{\beta} r)$$

where γ is a constant such that

$$\ln \gamma = - \int_0^{\infty} e^{-x} \ln x \, dx$$

$$= 0.577215670 \cdots\cdots , \text{ the Euler constant} \quad (2\text{-}28)$$

These forms of the singular basis functions are convenient for subsequent integral evaluations. The form chosen for the logarithmic basis function is such that, with $N_{\beta} = \sqrt{\frac{k_{\beta}^3}{\pi}}$, its normalization integral would have the simple value $(\frac{\pi^2}{6} + 1)$.

Since $$\ln(a \cdot 0) = \ln 0$$

and $$\ln(a \cdot 0) = \ln a + \ln 0$$

there is a certain amount of arbitrariness in deciding what actually is the finite part of a logarithmically divergent integral. It can be shown that this arbitrariness will not affect the values of the first-order molecular orbital coefficients provided only that the separation of

logarithmically divergent integrals into infinite and finite parts is made in such a way that all the infinite parts have the common factor $\ell n\, \epsilon$, where ϵ has the same value (tending to zero in the limit of a point magnetic dipole model of electrons and nuclei) for all the separated infinite parts.

In listing the finite parts of divergent integrals in Table II, each logarithmic divergence has been separated into a finite and an infinite part as follows:

$$\ell n\,(K\gamma r_0) \;=\; \ell n\, K + \ell n\,(\gamma r_0)$$

K is a linear combination of orbital exponents and varies from one divergent integral to another. $\ell n\, K$ gives rise to a contribution to the finite part of the divergent integral and $\ell n\,(\gamma r_0)$ is taken as the common divergent factor of the infinite parts of all logarithmically divergent integrals. The parameter r_0 is the value of the electron coordinate r in atomic units at the lower limit of integration and tends to zero in the limit of a point magnetic dipole model of electrons and nuclei.

The derivation of entry (4) in Table II is based on the following expression for the Laplacian of $\ell n\, r$:

$$\nabla^2 \ell n\, r \;=\; \frac{\delta(r)}{r} + \frac{1}{r^2}, \qquad r \geq 0 \tag{2-30}$$

The arguments used in the derivation of this expression are summarized in Appendix B.

2.4 Cusp conditions on the first-order molecular orbitals

In this section we shall derive the cusp conditions on the first-order molecular orbitals. The conditions may be derived from an analysis of the integro-differential equations which the exact first-order molecular orbitals obey. These equations may be obtained by applying the variational principle to the expression for $E'^{(2)}$ given by the first equality of equation (2-13). The cusp conditions are derivable from the resulting equation, namely

$$\left[h^0 + \sum_j (2 J_j^0 - K_j^0) - \epsilon_k^0 \right] \phi_k^1 + \left[h^1 - \sum_j (K_j^{0,1} + K_j^{1,0}) - \epsilon_k^1 \right] \phi_k^0 = 0 \tag{2-31}$$

where the notations of section 2.2 have been retained and the coulomb and exchange operators operating on the coordinates of, say, electron 2 are defined by

$$J_j^0(2) = \int dv_1 \; \phi_j^0(1) \; \phi_j^0(1) \frac{1}{r_{12}}$$

$$K_j^0(2) = \int dv_1 \; \phi_j^0(1) \frac{P_{12}}{r_{12}} \phi_j^0(1)$$

$$K_j^{1,0}(2) = \int dv_1 \; \phi_j^1(1) \frac{P_{12}}{r_{12}} \phi_j^0(1)$$

$$K_j^{0,1}(2) = \int dv_1 \; \phi_j^0(1) \frac{P_{12}}{r_{12}} \phi_j^1(1)$$

P_{12} being the operator which interchanges electrons 1 and 2.

The cusp conditions at the nuclear center of Fermi-contact perturbation are obtained by letting $r \to 0$ in (2-31). Near $r = 0$, (2-31) reduces to

$$h^0 \phi_k^1 + h^1 \phi_k^0 = 0; \qquad r \to 0 \tag{2-32}$$

We can always expand ϕ_k^0 and ϕ_k^1 in terms of spherical harmonics having origin at $r = 0$:

$$\phi_k^0 = \sum_{\ell=\ell'}^{\infty} \sum_{m=-\ell}^{\ell} r^\ell f_{\ell m}(r) Y_{\ell m} (\cos \theta, \phi) \tag{2-33}$$

$$\phi_k^1 = \sum_{\ell=\ell'}^{\infty} \sum_{m=-\ell}^{\ell} r^\ell g_{\ell m}(r) Y_{\ell m} (\cos \theta, \phi) \tag{2-34}$$

where ℓ' is the lowest value of ℓ appearing in the expansions. Then (2-32) gives

$$\left[-\frac{1}{2}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} \right) - \frac{Z_A}{r} + \frac{\ell(\ell+1)}{2r^2} \right] r^\ell g_{\ell m} + h^1 r^\ell f_{\ell m} = 0; \qquad r \to 0 \tag{2-35}$$

where Z_A is the charge of the nucleus A, the origin of the Fermi-contact perturbation.

For $\ell > 0$, the delta function in h^1 in equation (2-35) is multiplied by powers of r and therefore has no effect. Thus h^1 may be dropped from (2-35) when $\ell > 0$, giving

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{\ell(\ell+1)}{2r^2} - \frac{Z_A}{r} \right] r^{\ell} g_{\ell m} = 0; \quad \ell > 0, \; r \to 0 \tag{2-36}$$

A trial solution in the form of a power series

$$y = r^{\ell} g_{\ell m} = \sum_{n=0}^{\infty} a_n r^{n+s} \tag{2-37}$$

leads to

$$s = \ell$$

and

$$g_{\ell m}(r) = a_0 \left[1 - \frac{Z_A}{\ell+1} \cdot r + \cdots\cdots \right]; \quad \ell > 0 \tag{2-38}$$

This is identical in form to the well-known behaviour [26] of the unperturbed molecular orbital (2-33) near any nucleus with charge Z, namely

$$f_{\ell m}(r) = a_0' \left[1 - \frac{Z}{\ell+1} \cdot r + \cdots\cdots \right]; \quad \ell \geq 0, \; r \to 0 \tag{2-39}$$

The behaviour of $g_{\ell m}(r)$ for $\ell = m = 0$ and $r \to 0$ is different because the h^1 term may not be dropped. We have

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{Z_A}{r} \right] g_{00} + h^1 f_{00} = 0; \; r \to 0 \tag{2-40}$$

From the similarity between (2-40) and the equation (2-3) for the first-order wavefunction of the hydrogen atom near $r = 0$, we expect the solution for $g_{00}(r)$ to contain $\frac{1}{r}$ and $\ell n\, r$. Hence we write

$$g_{00}(r) = A_{-1}\frac{1}{r} + A_{\ell og}\,\ell n\, r + A_0 + A_1 r + A_2 r^2 + \cdots\cdots \qquad (2\text{-}41)$$

Inserting (2-41) and (2-39) into the left-hand side of (2-40) and equating coefficients on left- and right-hand sides gives

$$A_{-1} = -2 f_{00}(0)$$

and

$$A_{\ell og} = -2 Z_A A_{-1}$$

Hence

$$g_{0\,0}(r) = -2 f_{00}(0)\,(\frac{1}{r} - 2 Z_A\,\ell n\, r + \cdots\cdots); \qquad r \to 0 \qquad (2\text{-}42)$$

A similar analysis of equation (2-31) in the neighbourhood of a nucleus B away from the origin of the Fermi-contact perturbation giving rise to ϕ_k^1 yields

$$g_{\ell m}(r) = b\,(1 - \frac{Z_B}{\ell+1}\cdot r + \cdots\cdots); \quad \ell \geq 0, \; r \to 0 \qquad (2\text{-}43)$$

where the coordinates r, θ, and ϕ in the expansion (2-34) defining $g_{\ell m}(r)$ are now referred to nucleus B as origin.

The cusp value of ϕ_k^1 at a nucleus is defined as the ratio of the coefficient of the second leading term in $g_{\ell' m}(r)$ to the coefficient of

the leading term in the expansion of the wavefunction about that nucleus. Hence from the preceding paragraphs, we have the following theoretical conditions on the exact first-order molecular orbitals:

$$\text{Cusp value of } \phi_k^1 \text{ at nucleus A (origin of perturbation giving rise to } \phi_k^1) = \begin{cases} -\dfrac{Z_A}{\ell'+1}, & \ell' \neq 0 \\ -2\,Z_A, & \ell' = 0 \end{cases} \tag{2-44}$$

$$\text{Cusp value of } \phi_k^1 \text{ at nucleus B (away from nuclear origin of perturbation giving rise to } \phi_k^1) = -\frac{Z_B}{\ell'+1}, \quad \ell' \geq 0 \tag{2-45}$$

Except for the spherically symmetric component $\ell = \ell' = 0$, the theoretical conditions on the first-order molecular orbitals are therefore identical to those on the unperturbed molecular orbitals.[26]

3. Application to the HD molecule

The perturbation-variational approach of R. M. Pitzer has been applied to the calculation of the nuclear spin-spin isotropic coupling constant in the HD molecule. The calculation is based on a bond length of R = 1.4 a.u. for the molecule. This is very close to the experimentally found equilibrium bond length of $R = 0.7413_6$ A = 1.4010 a.u.[27]

3.1 Basis functions

The unperturbed electronic ground state of the molecule is represented by a minimal-basis-set wavefunction. That is, a single 1s Slater-type atomic orbital is used on each of the hydrogen and the deuterium nuclei. The value of the orbital exponent, chosen to minimize the total electronic energy of the unperturbed molecule,[20] is 1.1895 . The two basis functions are labelled as

$$\chi_1 = \sqrt{\frac{k^3}{\pi}}\, e^{-kr_H}$$

$$\chi_4 = \sqrt{\frac{k^3}{\pi}}\, e^{-kr_D}; \qquad k = 1.1895 \tag{3-1}$$

with χ_2, χ_3 (centered on H) and χ_5, χ_6 (centered on D) being anticipated additions to the basis set at some future date. Dropping molecular orbital subscripts since there is but one molecular orbital, the normalized unperturbed molecular orbital used in this research for the HD molecule is thus

$$\phi^0 = 0.5457\ 1763\ (\chi_1 + \chi_4) \tag{3-2}$$

This analytic representation of the unperturbed molecular orbital has a cusp value of -1.0003 compared to the value of -1.0 for the exact zero-order molecular orbital.

Two singular basis functions, one of each kind, have been included in the expansion of the first-order molecular orbital. They are labelled as follows:

$$\chi_7 = \sqrt{\frac{k^3}{\pi}} \frac{e^{-kr_H}}{kr_H}$$

$$\chi_8 = \sqrt{\frac{k^3}{\pi}} e^{-kr_H} \ell n (2 \gamma k r_H); \qquad k = 1.1895 \tag{3-3}$$

where γ is defined as in (2-28). We note that neither χ_7 nor χ_8 is normalized:

$$\int \chi_7 \chi_7 \, dv = 2$$

$$\int \chi_8 \chi_8 \, dv = \frac{\pi^2}{6} + 1 \tag{3-4}$$

The first-order molecular orbital takes the form

$$\phi_H^1 = C_1^1 \chi_1 + C_4^1 \chi_4 + C_7^1 \chi_7 + C_8^1 \chi_8 \tag{3-5}$$

where the subscripts in each first-order molecular orbital coefficient refer to the basis function. The literal subscript H denotes the origin of the perturbation.

3.2 Evaluation of integrals

3.2.1 Divergent integrals

Since both singular basis functions χ_7 and χ_8 have the same exponent, all logarithmically divergent integrals are found to diverge as $\ell n(2\gamma k r_0)$ where $r_0 \to 0$ is the parameter defined in section 2.3. Hence logarithmically divergent terms in the expression (2-13) for $E'^{(2)}$ will be grouped together with $\ell n(2\gamma k r_0)$ as common factor. The finite parts of divergent integrals then take the simple forms shown in Table III. This is to be contrasted to the general case (see Table II) where different exponents are present and logarithmic singularities appear as $\ell n(2\gamma k_1 r_0)$, $\ell n\,\gamma(k_1+k_2)r_0$, etc. In the general case, the only common logarithmically divergent factor is $\ell n(\gamma r_0)$:

$$\ell n(2\gamma k_1 r_0) = \ell n(2k_1) + \ell n(\gamma r_0)$$

$$\ell n[\gamma(k_1+k_2)r_0] = \ell n(k_1+k_2) + \ell n(\gamma r_0), \text{ etc.}$$

The parts $\ell n(2k_1)$, $\ell n(k_1+k_2)$, etc. have to be separated out and included in the finite parts of the integrals.

3.2.2 Finite integrals

In order to evaluate the finite molecular integrals encountered, various types of numerical quadrature have to be tested on integrals involving the logarithmic function. The simple integral

$$\int_0^\infty e^{-t}\, \ell n(\gamma t)\, dt \qquad (3\text{-}6)$$

Table III. Finite parts of divergent integrals encountered in the calculation of the nuclear spin-spin coupling constant in HD [a]

Divergent integral	Finite part
$\langle \chi_7 \left\| \frac{\delta(r)}{r^2} \right\| \chi \rangle$	$-(r\,\chi_7)_{r=0}\,(\chi)_{r=0} \cdot 4\pi$
$\langle \chi_8 \left\| \frac{\delta(r)}{r^2} \right\| \chi \rangle$	0
$\langle \chi_7 \left\| -\frac{1}{2}\nabla^2 \right\| \chi_7 \rangle$	$-5\,k^2$
$\langle \chi_8 \left\| -\frac{1}{2}\nabla^2 \right\| \chi_7 \rangle$	$-\frac{1}{2}\,k^2$
$\langle \chi_7 \left\| -\frac{1}{2}\nabla^2 \right\| \chi_8 \rangle$	$-\frac{1}{2}\,k^2$
$\langle \chi_7 \left\| -\frac{Z}{r} \right\| \chi_7 \rangle$	0

[a] χ is any basis function that is finite at $r = 0$.

was first studied. This integral has been chosen since, of all the types of integrals encountered, it has the most extreme kind of an integrand for which a polynomial approximation may not be adequate. Although the integral is finite, the integrand has a singularity at the origin. This type of integral always occur in an electron-repulsion integral whenever both singular basis functions are present as functions of the same electron coordinate. We have

$$\int \frac{e^{-kr_1}}{r_1} e^{-kr_1} \ell n(2\gamma k r_1) \frac{1}{r_{12}} dv_1$$

$$= \int_{\phi_1=0}^{2\pi} \int_{\cos\theta_1=-1}^{1} \int_{r_1=0}^{\infty} \frac{e^{-2kr_1}}{r_1} \ell n(2\gamma k r_1) \frac{1}{r_>} r_1^2 dr_1 \, d(\cos\theta_1) \, d\phi_1$$

$$= 4\pi \left[\frac{1}{r_2} \int_0^{r_2} e^{-2kr_1} \ell n(2\gamma k r_1) \, r_1 dr_1 + \int_{r_2}^{\infty} e^{-2kr_1} \ell n(2\gamma k r_1) \, dr_1 \right] \tag{3-7}$$

In the second equality above, use has been made of the multipole expansion for $\frac{1}{r_{12}}$ as given in equation (3-4) of Thesis Part I. $r_>$ is the greater of r_1 and r_2. The second integral in the square brackets of (3-7) gives rise to an integral of the form (3-6) for small values of r_2, the coordinate of integration over the second electron.

The integrand of (3-6) has the qualitative form shown in Figure 1. The integrand gives a negative contribution to the integral in the interval $0 \leq t \leq \frac{1}{\gamma}$ and a positive contribution in the remaining interval. These contributions should have the same magnitude since the exact

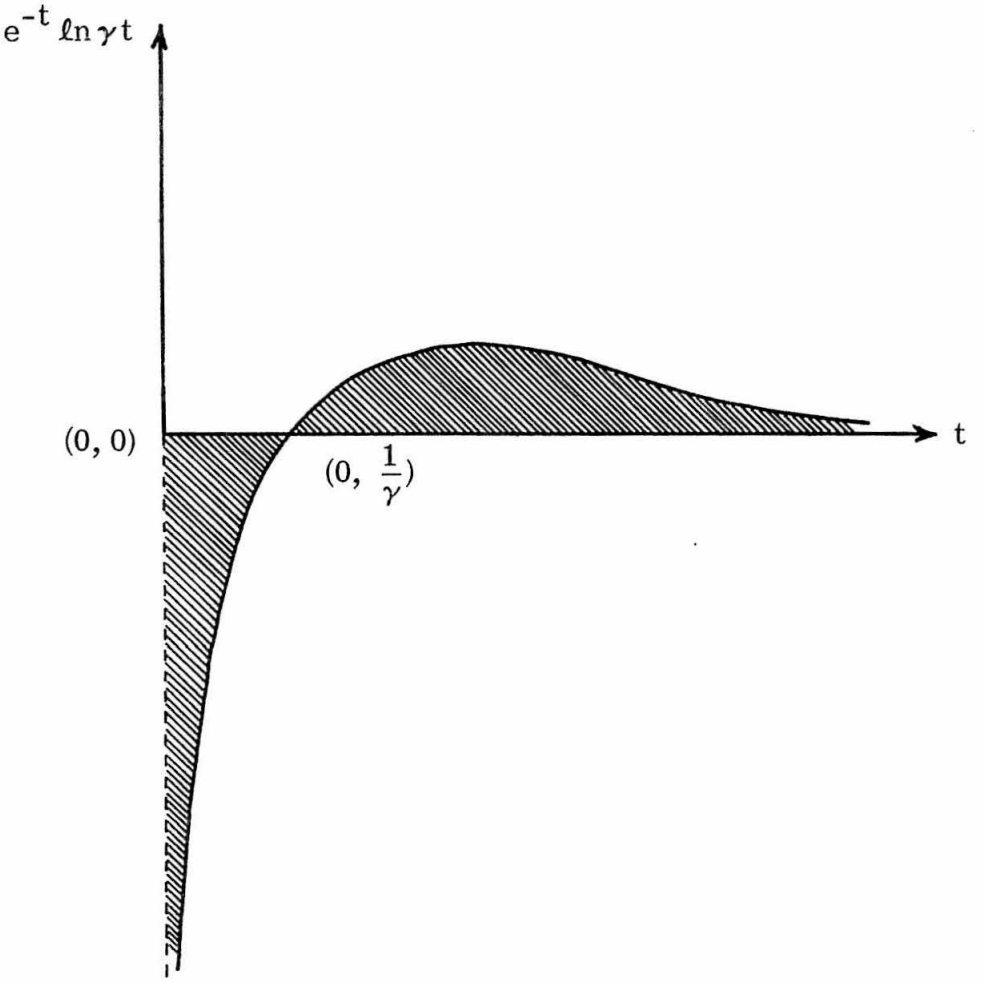


Figure 1. Qualitative form of the function $e^{-t} \ln \gamma t$

value of the integral is zero.

In table IV, we list some typical values calculated for the positive and negative parts of this integral using various types of quadrature, as well as the accurate values obtained with a computer program written by J. B. Hughes.[28] The table shows that Gauss-Legendre and Gauss-Laguerre quadratures[29] are clearly unsuitable for this kind of an integral.

It is possible to construct quadrature formulas based on polynomials $G_n(t)$ orthonormal with respect to $\ell n\, t$ as weight function in the interval $0 \leq t \leq 1$. Such polynomials up to degree 4 can be found exactly and have been given by H. Berthod-Zaborowski[30] together with the ordinates and weights for numerical quadrature based on these polynomials. The determination of the coefficients in the higher order polynomials cannot be done exactly and requires approximate numerical techniques. Approximate ordinates and weights for numerical quadrature based on polynomials $G_n(t)$ up to degree 16 have been given by Stroud and Secrest.[31] In the next-to-last column of Table IV, we have given the calculated contribution to the integral (3-6) from the range $0 \leq t \leq \frac{1}{\gamma}$ using an 8-point quadrature based on the data of Stroud and Secrest. The result obtained agrees very well with the accurate value. In conjunction with a 56-point Gauss-Legendre and Gauss-Laguerre quadrature for the range $\frac{1}{\gamma} \leq t \leq \infty$, this gives a highly accurate value for the entire integral.

Where the logarithmic singularity at $t = 0$ is weakened by the presence of a linear or higher power in t in the integrand, we have

Table IV. Typical results obtained in evaluating the integral (3-6) using various types of quadrature compared with accurate values [a]

Range	Value and method used	Value and method used	Value and method used	Accurate value
$(0, \frac{1}{\gamma})$	-0.49092720 G-LGN(24)	-0.49118606 G-LGN(32)	-0.49153429 L-Q(8)	-0.49153424
$(\frac{1}{\gamma}, \infty)$	0.49155335 G-LGN(12) + G-LGR(6)	0.49153744 G-LGN(16) + G-LGR(8)	0.49153406 G-LGN(48) + G-LGR(8)	0.49153424
$(0, \infty)$	0.000626	0.000351	-0.00000023	0.

[a] G-LGN: Gauss-Legendre quadrature
G-LGR: Gauss-Laguerre quadrature
L-Q : Quadrature based on polynomials orthonormal with respect to the logarithm function as weight function, References 30 and 31.

Parentheses indicate number of points taken in the quadrature.

found that Gauss-Legendre and Gauss-Laguerre quadratures give accurate results. This indicates that the difficulty encountered with the integral (3-6) is not due to the presence of the logarithm function itself but rather is associated with the difficulty in approximating an integrand having a singularity by means of a simple polynomial of finite degree.

Although workable numerical quadrature techniques have thus been found for the new kinds of molecular integrals, we have decided in practice to evaluate all integrals of the types

$$\int_0^x t^{n+1} (\ell n\, \gamma t)^{n_\ell - 1} e^{-t}\, dt$$

$$\int_x^\infty t^{n-1} (\ell n\, \gamma t)^{n_\ell - 1} e^{-t}\, dt\,; \qquad n \geq 1,\ n_\ell \geq 1 \tag{3-8}$$

by using analytical means since a computer program for such a purpose has already been written by Prof. R. M. Pitzer on the basis of analytical formulas developed by M. Geller.[32] We note that

$$\int_{-x}^\infty \frac{e^{-t}}{t}\, dt = - e^{-x} \ell n x + \int_x^\infty e^{-t} \ell n\, t\, dt \tag{3-9}$$

so that all single-center one-electron parts of electron repulsion integrals can be computed using the above mentioned program. In addition, the program can also be used to calculate the off-center nuclear attraction integral $\langle A \left| \frac{1}{r_B} \right| A \rangle$.

Most of the new kinds of molecular integrals have therefore been evaluated in this research using a combination of analytical methods and numerical quadratures. Integrals involving orbitals on different centers were computed by means of the zeta function method described in section 3.1 of Thesis Part I, the expansion center being the H-nucleus where the singular basis functions are located. The infinite series arising from the two-center exchange integrals converged rapidly and no transformation of any kind on the series was necessary.

Wherever possible, integral values obtained using the foregoing procedures were compared with exact values obtained by Professor R. M. Pitzer without using numerical quadrature. Where comparisons with exact values were not possible, check values for electron repulsion integrals were obtained by reversing the order of integration, that is, by integrating over the coordinates of electron 2 first instead of electron 1, or vice versa.

3.3 Results and discussion

We give in Table IVa and IVb all integral values found in this research. Entries given for divergent integrals are values of their finite parts as defined in section 3.2.1.

Using these integral values, equations (2-15), (2-21), and (2-27) are treated as a system of simultaneous equations linear in the unknowns consisting of first-order molecular orbital coefficients and Lagrange multipliers. The simultaneous equations are solved by matrix inversion and the solutions found are given in Table V. The results previously obtained[20] without using the logarithmic basis

Table IVa. Values of one-electron molecular integrals employed in the perturbation-variational calculation on the HD molecule. Labels of basis functions are as explained in the text.

ONE-CENTER INTEGRALS

		S	V	T
8	8	0.26449340E 01	-0.19566491E 01	0.18711721E 01
8	7	0.99999838E 00	0.	-0.70745513E 00
8	1	0.15000001E 01	-0.11894981E 01	0.35372525E-00
7	7	0.19999997E 01	0.	-0.70745512E 01
7	1	0.99999993E 00	-0.23789997E 01	0.21223649E 01
1	1	0.99999996E 00	-0.11894999E 01	0.70745505E 00
4	4	0.99999999E 00	-0.11894999E 01	0.70745513E 00

TWO-CENTER INTEGRALS

		S	VA	VB	T
4	1	0.67893548E 00	-0.59962527E 00	-0.59962524E 00	0.23293788E-00
7	4	0.50409859E 00	-0.78893112E 00	-0.44994953E-00	0.17858788E-00
8	4	0.12754761E 01	-0.76559616E 00	-0.94428542E 00	0.30654708E-00

TWO-CENTER NUCLEAR ATTRACTION INTEGRALS

8	8	-0.15296166E 01
8	7	-0.65756673E 00
8	1	-0.91594466E 00
7	7	-0.14184056E 01
7	1	-0.6887347CE 00
1	1	-0.64618421E 00
4	4	-0.64618421E 00

H1 INTEGRALS

1	1	0.67321429E 01
4	1	0.12732764E 01
7	1	-0.13464285E 02
4	4	0.24081974E-00
7	4	-0.12732764E 01

Table IVb. Values of two-electron molecular integrals employed in the perturbation-variational calculation on the HD molecule. Labels of basis functions are as explained in the text.

8	8	4	1	0.99302775
8	7	4	1	0.44293506
8	4	8	1	0.97423343
8	1	7	4	0.51067597
8	1	4	1	0.60347863
7	7	4	1	1.12039609
8	4	7	1	0.75806794
7	4	7	1	0.49220914
7	1	4	1	0.50342083
8	4	1	1	0.69528960
7	4	1	1	0.39600462
4	1	1	1	0.44247358
8	8	1	1	1.58134130
8	7	1	1	0.73324854
8	1	8	1	1.34131590
8	1	7	1	1.09824960
8	1	1	1	0.97828057
7	7	1	1	2.10849318
7	1	7	1	1.18949990
7	1	1	1	0.89212497
1	1	1	1	0.74343760
4	4	4	4	0.74343760
8	4	4	4	0.75002845
7	4	4	4	0.33999337
4	4	4	1	0.44247372
8	8	4	4	1.32579999
8	7	4	4	0.56273038
8	1	4	4	0.78897724
7	7	4	4	1.26146439
7	1	4	4	0.60011718
4	4	1	1	0.55741654
4	1	4	1	0.30421472
7	4	7	4	0.22737820
8	4	8	4	0.82644586
8	4	7	4	0.39568619
7	4	4	1	0.25242043
8	4	4	1	0.49645272

Table V. First-order molecular orbital coefficients and Lagrange multipliers obtained as solutions to the Pitzer equations [a]

Basis functions	ϕ_H^1	
	I	II
χ_1	-9.954656	-10.413533
χ_4	11.337698	9.116926
χ_7	-1.543808	-1.543808
χ_8		1.620968
ϵ^1	3.055234	3.503636
λ	-1.295589	-1.420249

[a] I: without using the logarithmic basis function.
II: using both singular basis functions.

function have also been included in the table.

The nuclear spin-spin coupling constant in cycles per second is given by the relation

$$J_{HD} = \frac{2\times 2}{h}\left(\frac{g_S \beta \beta_N}{3 a_0^3}\right)^2 \cdot \frac{m a_0^2}{h^2} \cdot g_H g_D \langle \phi_H^1 | \frac{\delta(r_D)}{r_D^2} | \phi^0 \rangle \qquad (3\text{-}10)$$

where β_N is the nuclear magneton, a_0 the Bohr radius, g_H and g_D the nuclear g factors, and r_D the integration variable referred to the D nucleus as origin; all remaining symbols have meanings given previously.

The calculated value of J_{HD} is found to be +96.6 cps. As summarized in Table VI, this represents an improvement over the calculated value of +120 cps obtained previously[20] without using the logarithmic basis function but it is still about a factor of two too large compared with the experimental value of $+43.0 \pm 0.5$ cps.

Table VI also gives the cusp values of the first-order molecular orbital at both the H and D nuclei. These cusp values have been defined in equations (2-44) and (2-45) and their exact theoretical values are -2 and -1 at the H and D nuclei, respectively. The cusp conditions are clearly poorly satisfied in the first-order molecular orbital calculated both with and without the logarithmic basis functions. It is of interest to note that the cusp value at the D nucleus is almost unaffected by the addition of a logarithmic basis function on the H nucleus.

Table VI. Values of the nuclear spin-spin coupling constant and energy quantities calculated for the HD molecule (I) without using the logarithmic basis function, and (II) using both singular functions

	I[a]	II	Experimental measurement or theoretical condition
J_{HD} (cps)	+120	+96.6	$+ 43.0 \pm 0.5$[b]
Cusp value at H		-1.2490	-2.0
Cusp value at D	-1.4533	-1.4425	-1.0
$E_f^{(2)}$ (a.u.)	-130.5243	-120.7245	

[a] Reference 20.

[b] Reference 8.

The quantity $E_f^{(2)}$ listed in the last row of Table VI is the finite part of the second-order self coupling energy

$$E^{(2)} = 4 \langle \phi_H^1 | h_H^1 | \phi^0 \rangle + 2 \langle \phi_H^1 | h^0 | \phi_H^1 \rangle + \langle \phi_H^1 | 2J^0 - 4K^0 | \phi_H^1 \rangle \qquad (3\text{-}11)$$

which, as shown in Appendix C, may be re-written in the form

$$E^{(2)} = 2\{(\phi_H^1 | h_H^1 | \phi^0) - 2\lambda(\phi^0)_{r=0} + \epsilon^0(\phi_H^1 | \phi_H^1)\} \qquad (3\text{-}12)$$

In these expressions, the origin of the perturbation has been explicitly emphasized by means of a literal subscript on both the first-order molecular orbital and on the perturbational Hamiltonian. The operators J^0 and K^0 have been defined in connection with (2-31). λ is the Lagrange multiplier occurring in equation (2-21) and ϵ^0 the unperturbed orbital energy. A numerical subscript referring to the molecular orbital has been suppressed in ϕ_H^1, ϕ^0, J^0, K^0, λ, and ϵ^0.

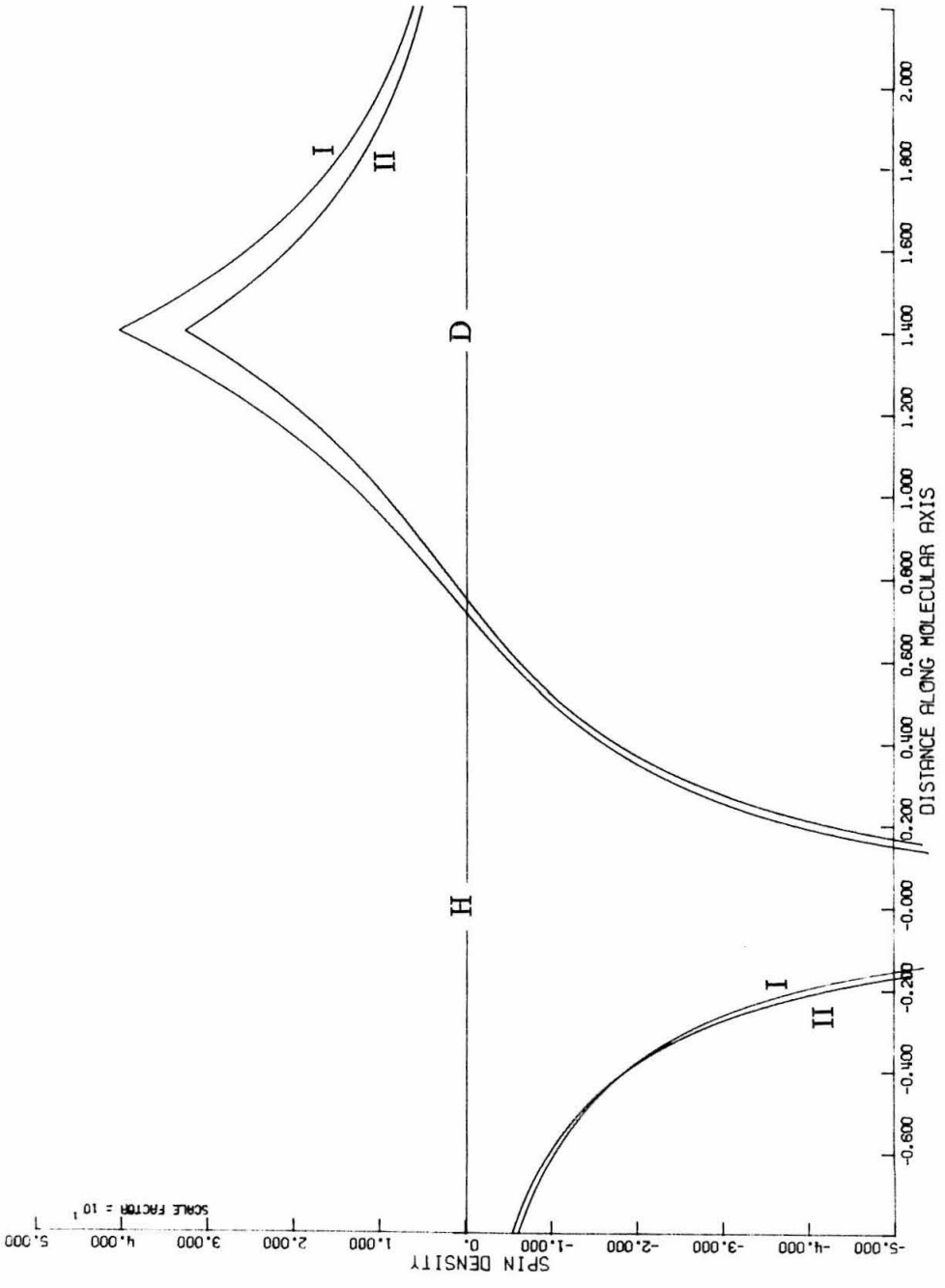
The apparent increase in the value of $E_f^{(2)}$ upon addition of a logarithmic function to the basis set causes no concern in view of the fact that the logarithmically divergent part of the energy arising from the logarithmic basis function has a negative sign, as can be seen from (2-17). In general, a comparison of the finite parts of the second-order energy obtained with two different basis sets requires considerable care and may not be meaningful.

In Figure 2, the induced spin density

$$\rho(\vec{R}) = 4 \langle \phi_H^1 | \delta(\vec{r} - \vec{R}) | \phi^0 \rangle \qquad (3\text{-}13)$$

calculated using the first-order molecular orbital obtained in this research is plotted as a function of R, the position along the HD internuclear axis. On the same plot, the induced spin density function previously found[20] without using the logarithmic basis function is given for comparison. The induced spin density at the D nucleus is directly proportional to the nuclear spin-spin coupling constant, as is evident from a comparison of (3-10) and (3-13). The decreased peak of the induced spin density function at the D nucleus upon the addition of the logarithmic basis function is therefore reflected in the decrease in the calculated coupling constant from +120 cps to +96.6 cps.

Figure 2. The indiced spin density in the HD molecule as a function of position along the internuclear axis calculated (I) without using the logarithmic basis function and (II) using both singular basis functions.


I
II
D
H
I
II
-0.600
-0.400
-0.200
-0.000
0.200
0.400
0.600
0.800
1.000
1.200
1.400
1.600
1.800
2.000
DISTANCE ALONG MOLECULAR AXIS
-5.000
-4.000
-3.000
-2.000
-1.000
0.
1.000
2.000
3.000
4.000
5.000
SPIN DENSITY
SCALE FACTOR = 10 1

4. Conclusion

This thesis research shows the practicality of the perturbation-variational approach to the calculation of nuclear spin-spin coupling constants. In particular, it has been found that the new kinds of molecular integrals encountered can be evaluated without great difficulty. However, the calculated value of +96.6 cps for the nuclear spin-spin coupling constant in HD is disappointing compared with the experimental value of $+43.0 \pm 0.5$ cps. Since the coupling constant is clearly sensitive to the unperturbed electron density at both coupled nuclei [see equations (2-15) and (3-10)] an accurate description of the unperturbed electronic wavefunction is essential. Prior to the addition of more basis functions of the conventional type to the wavefunction, we are therefore unable to arrive at a concrete conclusion as to whether or not a refinement of the present theory or the inclusion of electron correlation in the wavefunction would be necessary.

Appendix A. The first-order wavefunction of the hydrogen atom perturbed by Fermi-contact interaction

From equation (2-3), the equation for the first-order wavefunction of the hydrogen atom perturbed by Fermi-contact interaction is

$$(-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \frac{Z^2}{2})\psi^1 = -\left(\frac{\delta(r)}{r^2} - 4Z^3\right)\sqrt{\frac{Z^3}{\pi}}\, e^{-Zr} \qquad \text{(A-1)}$$

Now[33]

$$\nabla^2 \frac{1}{r} = -4\pi\,\delta(\vec{r})$$

$$= -\frac{\delta(r)}{r^2} \qquad \text{(A-2)}$$

Therefore we look for a solution of the form

$$\psi^1 = \sqrt{\frac{Z^3}{\pi}}\,(-\frac{2}{r} + f)\, e^{-Zr} \qquad \text{(A-3)}$$

so that (A-1) becomes, after simplification,

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - 2Z\frac{d}{dr}\right)f = \frac{4Z}{r^2} - 8Z^3 \qquad \text{(A-4)}$$

Let

$$\frac{df}{dr} = f' = g \qquad \text{(A-5)}$$

Then

$$g' + (\frac{2}{r} - 2Z)g = \frac{4Z}{r^2} - 8Z^3 \qquad \text{(A-6)}$$

The integrating factor for this first-order differential equation is $r^2 e^{-2Zr}$ and we have

$$r^2 e^{-2Zr} g = 4Z^2 r^2 e^{-2Zr} + 4Z\, r e^{-2Zr} + K \qquad \text{(A-7)}$$

where K is an integration constant.

From the boundary condition that ψ^1 must be zero as $r \to \infty$, we have $\frac{\partial \psi^1}{\partial r} \to 0$ as $r \to \infty$. This gives

$$\lim_{r \to \infty} r^2 e^{-2Zr} g = 0 \qquad \text{(A-8)}$$

so that $K = 0$.

Therefore
$$g = 4Z^2 + 4Z \cdot \frac{1}{r} \qquad \text{(A-9)}$$

and
$$f = 4Z^2 r + 4Z \ln r + C \qquad \text{(A-10)}$$

Hence,
$$\psi^1 = \sqrt{\frac{Z^3}{\pi}} \cdot 2 \left(-\frac{1}{r} + 2Z \ln r + 2Z^2 r + C\right) e^{-Zr} \qquad \text{(A-11)}$$

The constant of integration C may be chosen to be $C = Z[2Z \ln(2\gamma Z) - 5]$ so that $(\psi^0 + \psi^1)$ is normalized to first order.

We note that the solution (A-11) will satisfy (A-1) only if we take

$$\nabla^2 \ln r = \frac{1}{r^2}$$

for all values of r including $r = 0$. If the Laplacian of $\ln r$ is taken as given by equation (B-7) of Appendix B, then the insertion of the right-hand-side of (A-11) into the left-hand-side of equation (A-1) gives

$$\left(-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \frac{Z^2}{2}\right)\psi^1 = -\left(\frac{\delta(r)}{r^2} + 2Z\frac{\delta(r)}{r} - 4Z^3\right)\sqrt{\frac{Z^3}{\pi}}\,e^{-Zr} \tag{A-12}$$

which differs from the right-hand-side of (A-1) in the appearance of a second delta function term. This apparent difference has no significance inasmuch as the Fermi-contact interaction Hamiltonian could have a second delta function term, namely

$$\mathcal{H}^1 = \frac{8\pi}{3} g_S \beta \sum_{k,N} \gamma_N \hbar \left[\delta(\vec{r}_{kN}) + 2Z r_{kN}\,\delta(\vec{r}_{kN})\right] \vec{S}_k \cdot \vec{I}_N \tag{A-13}$$

without violating Fermi's original derivation of the interaction.[6] In this case, the right-hand-side of (A-1) would be identical to that of (A-12).

Appendix B. The Laplacian of $\ell n\, r$

This appendix gives the arguments used in arriving at the form (2-30) for the Laplacian of $\ell n\, r$. The arguments start from Poisson's equation in cgs units:

$$\nabla^2 \Phi = -4\pi\rho \tag{B-1}$$

where Φ is the electrostatic potential and ρ the charge density.

For a line charge

$$\Phi(r) = -2.d.(\ell n\, r - \ell n\, r_0) \tag{B-2}$$

where r is the perpendicular distance from the line charge, d the charge per unit length of the line charge, and the arbitrary zero level of potential is set at $r = r_0$. Integrating both sides of (B-1) over a cylindrical volume element enclosing the line charge and having length L and radius a gives

$$-d. \int_0^{2\pi} \int_0^a \int_0^L 2[\nabla^2(\ell n\, r - \ell n\, r_0)]\, dz\, r\, dr\, d\phi = -4\pi.d.L \tag{B-3}$$

where r, z, and ϕ are cylindrical coordinates. This simplifies to

$$\int_0^a r\left(\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr}\right) \ell n\, r\, dr = 1 \tag{B-4}$$

Hence

$$\left(\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr}\right) \ell n\, r = \frac{\delta(r)}{r} \tag{B-5}$$

where the Dirac delta function is defined such that

$$\int_0^b \delta(r)\, dr = 1; \qquad b > 0 \tag{B-6}$$

Equation (B-5) is a mathematical identity and holds for any variable r including the radial spherical coordinate. Therefore, in spherical coordinates,

$$\begin{aligned} \nabla^2 \ell n\, r &= \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \ell n\, r \\ &= \left(\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} \right) \ell n\, r + \frac{1}{r} \frac{d}{dr} \ell n\, r \\ &= \frac{\delta(r)}{r} + \frac{1}{r^2}; \qquad r \geq 0 \end{aligned} \tag{B-7}$$

Appendix C. The second-order self-coupling energy in HD

This appendix gives the derivation of the equation (3-12) which is the actual form in which the finite part of the second-order self-coupling energy of HD is computed.

Multiplication of Pitzer's second equation (2-21) by $C^1_{\gamma k}$ and summing over γ gives

$$\sum_\gamma \Big\{ C^1_{\gamma k} h^1_{\gamma k} - \epsilon^1_k C^1_{\gamma k} S_{\gamma k} + \sum_\alpha (C^1_{\gamma k} f^0_{\gamma\alpha} - \epsilon^0_k C^1_{\gamma k} S_{\gamma\alpha}) C_{\alpha k} - \sum_{\alpha i} C^1_{\gamma k} C^1_{\alpha i} [(\gamma\alpha|ik) + (\gamma i|k\alpha)] \Big\} = \sum_\gamma \lambda_k C^1_{\gamma k} (r\chi_\gamma)_{r=0} \tag{C-1}$$

If there is only one occupied molecular orbital, as in the HD molecule, then (C-1) becomes (dropping the M.O. label)

$$(\phi^1|h^1|\phi^0) - \epsilon^1(\phi^1|\phi^0) + (\phi^1|f^0|\phi^1) - \epsilon^0(\phi^1|\phi^1) - (\phi^1|J+K|\phi^1) = \lambda(r\phi^1)_{r=0} \tag{C-2}$$

Hence

$$\lambda = \frac{1}{(r\phi^1)_{r=0}} \Big[(\phi^1|h^1|\phi^0) + (\phi^1|h^0 + 2J^0 - K^0 - J^0 - K^0|\phi^1) - \epsilon^0(\phi^1|\phi^1) \Big] \tag{C-3}$$

$$= -\frac{1}{2}\cdot\frac{1}{(\phi^0)_{r=0}}\Big[(\phi^1|h^1|\phi^0) + (\phi^1|h^0 + J^0 - 2K^0|\phi^1) - \epsilon^0(\phi^1|\phi^1)\Big] \qquad \text{(C-3)}$$

The last step made use of equation (2-15).

From (3-11), we have

$$E^{(2)} = 4(\phi^1|h^1|\phi^0) + 2(\phi^1|h^0|\phi^1) + (\phi^1|2J^0 - 4K^0|\phi^1)$$

$$= 2\{(\phi^1|h^1|\phi^0) - 2(-\tfrac{1}{2})[(\phi^1|h^1|\phi^0) + (\phi^1|h^0|\phi^1) + (\phi^1|J^0 - 2K^0|\phi^1)]\}$$

$$= 2\{(\phi^1|h^1|\phi^0) - 2[(\phi^0)_{r=0}\cdot\lambda - \tfrac{1}{2}\epsilon^0(\phi^1|\phi^1)]\}$$

$$= 2\{(\phi^1|h^1|\phi^0) - 2\lambda(\phi^0)_{r=0} + \epsilon^0(\phi^1|\phi^1)\} \qquad \text{(C-4)}$$

which is identical to (3-12).

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PROPOSITIONS

I. The Proton-Proton Distances in the Ferrocene Molecule from the Second Moment of the Nuclear Magnetic Resonance Spectrum

II. The Sign of the Electric Dipole Moment in the Carbon Monoxide Molecule

III. The Vibrational Force Constant and the Equilibrium Bond Length of the Hydrogen Molecule

IV. The Stability and Structure of Bound Molecular Dimers in Gaseous Hydrogen and Oxygen

V. The Position and Height of the Potential Maximum in $He_2(1s^2,\ 1s\,2s;\ {}^3\Sigma_u^+)$

PROPOSITION I The Proton-Proton Distances in the Ferrocene Molecule from the Second Moment of the Nuclear Magnetic Resonance Spectrum

The feasibility of determining the proton-proton distances in ferrocene from the second moment of the nuclear magnetic resonance spectrum is proposed.

X-ray studies[1] have located the positions of the iron and carbon atoms in the ferrocene molecule. Owing to their low scattering power, the exact locations of the hydrogen atoms remain unknown, although they have been depicted[2] as lying outside the two planes of the carbon rings. The molecular structure has therefore not been completely elucidated.

Free rotation of the two rings relative to each other in ferrocene has been predicted[3] and largely confirmed in the vapour phase[4] and in solution.[5] A small potential barrier similar to that in ethane cannot be ruled out.[6] Steric contribution, though small by itself, may form a significant fraction of such a low barrier, hence a reason for knowledge of the proton positions.

Ferrocene has previously been subjected to NMR studies in the solid state by Mulay et al.[7] and by Holm et al.[8] The narrow line width at room temperature obtained by the former group of workers was taken as evidence for rotation of the rings. The second group, however, interpreted results as supporting no reorientation of the cyclopentadienyl rings around the fivefold axis between 300°K and

110°K.

In their study of polycrystalline benzene Andrew and Eades [9] found convincing evidence that motion of the benzene rings occurs only above 70°K. At sufficiently low temperatures, it is therefore probable that motion of the cyclopentadienyl rings in ferrocene would likewise be frozen out.

Since Pake's pioneering work, [10] nuclear magnetic resonance has been applied a great deal to structural problems. From apparently shapeless humps in the nuclear magnetic resonance spectra of solids, accurate values for structural parameters have been obtained. Andrew and Eades [9] determined the distance between adjacent protons in benzene after ingeniously finding the intramolecular contributions to the NMR second moment. By extending the spirit of their work, one might wonder whether the intra- and inter-ring contributions to the second moment in the ferrocene molecule may not be found, leading to values for the proton-proton distances in this molecule. In this proposition, we show that this is indeed possible. Although more than one structural parameter cannot usually be obtained from a study of polycrystalline samples, it will be seen that this is not the case in ferrocene.

The key step in Van Vleck's derivation of the expressions for the NMR second moment [11] was utilizing the invariance of the trace of a matrix under a unitary transformation. If I stands for the spin of the nuclear species at resonance and I′ that of any other species of nuclei, then the contributions to the NMR second moment from like

and unlike species of nuclei are respectively

$$S(I;I) = \frac{3}{4}\gamma_I^4 \hbar^2 \frac{I(I+1)}{N} \sum_{j \neq k} \frac{(1 - 3\cos^2\theta_{jk})^2}{r_{jk}^6}$$

$$S(I;I') = \frac{1}{3}\gamma_I^2 \gamma_{I'}^2 \hbar^2 \frac{I(I+1)}{N} \sum_{j,\ell} \frac{(1 - 3\cos^2\theta_{j\ell})^2}{r_{j\ell}^6}$$

where γ_I and $\gamma_{I'}$ are the magnetogyric ratios for nuclear species I and I'

N is the total number of spins I

j, k are labels for nuclei of spin I

ℓ is the label for nuclei of spins I'

and θ_{jk} is the angle between the magnetic field direction and the line joining nuclei j and k;

the summations extend over all nuclei in the sample. Methods have been developed to correct for any torsional oscillations.[12] The total second moment is given by $S = S(I;I) + S(I;I')$.

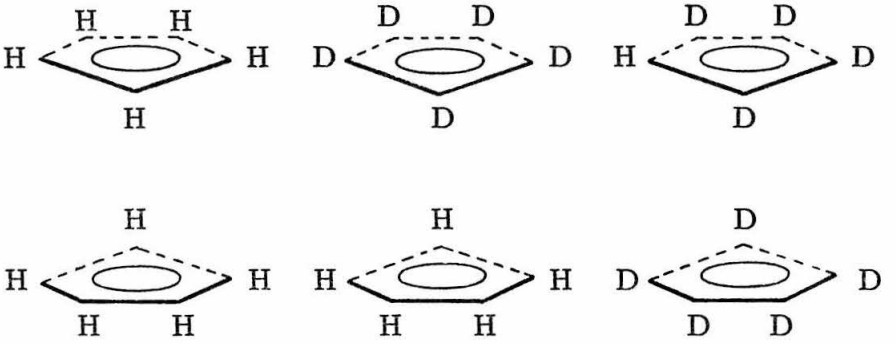
On replacing a nucleus of spin I in any site by one of spin I', the contribution of this site to the second moment is just the old contribution times the following factor:

$$\frac{4}{9} \frac{\gamma_{I'}^2 I'(I'+1)}{\gamma_I^2 I(I+1)}$$

If I and I′ are the spins of H and D nuclei, this ratio is

$$\alpha = 0.0236$$

The deuteron derivatives of ferrocene which will effect a separation of intra- and inter-ring contributions to the second moment are found to be I, II, and III as shown below:



I (S) II (S′) III (S″)

In the following discussion, a single subscript, 1 or 2, indicates the total intra- or inter-molecular contributions respectively to the proton NMR second moment. Let

S_{11} = intra-ring contribution of each proton to S_1

S_{12} = inter-ring contribution of each proton to S_1

S = second moment of proton resonance line in ferrocene

S' = second moment of proton resonance line in II, where all five of the H-atoms in one of the two rings have

been replaced by deuterons

S'' = second moment of proton resonance line in III, where all but one of the H-atoms have been replaced by deuterons

The iron isotope Fe^{57} has a magnetic moment. However, its natural abundance (2.245%) and magnetic moment (0.05 nuclear magnetons) are very small. Hence the effect of the iron nucleus on the NMR spectrum may be neglected. Then from the figures, it is seen that

$$S_1 = 10\,(S_{11} + S_{12}) \tag{1}$$

$$S_1' = 5\,(S_{11}' + S_{12}') = 5\,(S_{11} + \alpha S_{12}) \tag{2}$$

$$S = S_1 + S_2 \tag{3}$$

$$S'' = S_1'' + S_2'' = \frac{\alpha}{10} S_1 + \left(\frac{1}{10} + \frac{9}{10}\alpha\right) S_2 \tag{4}$$

$$S' = S_1' + S_2' = S_1' + \left(\frac{1}{2} + \frac{\alpha}{2}\right) S_2 \tag{5}$$

From the experimental values for S, S', and S'', (3), (4), and (5) may be solved for S_1 and S_1' which are then substituted in (1) and (2) to get S_{11} and S_{12}. From these two quantities, the evaluation of the two unknown structural parameters (h, the distance between the two planes containing the proton rings and a, the distance between adjacent protons in the same ring) is essentially a problem in elementary geometry.

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PROPOSITION II The Sign of the Electric Dipole Moment in the Carbon Monoxide Molecule

It is proposed that the existing experimental determination of the sign of the electric dipole moment in the carbon monoxide molecule suffers from the same inherent uncertainty as the ab initio calculations.

The sign of the electric dipole moment in the carbon monoxide molecule was determined by Rosenblum, Nethercot, and Townes[1] in 1958 using a method proposed by Townes et al.[2] It was apparently the first measurement of the sign of the electric dipole moment in any molecule. The sign was found to be C^-O^+.

In 1964, Huo[3] determined the sign from ab initio calculation and found it to be C^+O^- in disagreement with experiment. Since her calculation was based on an electronic wavefunction which is very near the Hartree-Fock limit, the disagreement between theory and experiment has aroused considerable interest.[4] However, it is known that the ab initio calculation involves taking the difference between electronic and nuclear contributions which are nearly equal in magnitude since the net dipole moment is very small. Therefore, a relatively small error in calculating the electronic contribution could give an opposite sign of the dipole moment. This has apparently been confirmed by a recent configuration-interaction calculation[5] (based on Huo's ground-state determinantal wavefunction) which resulted in a dipole moment -0.17 D (C^-O^+) in agreement with experiment.

We propose that the inherent inaccuracy present in the ab initio calculations is also present in the experimental determination from the isotopic variation of the rotational magnetic moment.

The rotational magnetic moment along a principal axis x of inertia may be written as [2]

$$\mu_x = M_{xx} \frac{\hbar J_x}{I_x} + M_{xy} \frac{\hbar J_y}{I_y} + M_{xx} \frac{\hbar J_z}{I_z} \tag{1}$$

where M_{xx}, etc., are components of a tensor as given by Townes et al.[2] and are functions of the electronic structure of the molecule. J_x, etc., are components of the rotational angular momentum along the principal axes of inertia and I_x, etc., the principal moments of inertia. For a diatomic molecule, the principal axes of the tensor M coincide with the principal axes of inertia. Therefore

$$I_x \mu_x = \hbar J_x M_{xx} \tag{2}$$

Upon isotopic substitution, we have, considering the same rotational state before and after substitution,

$$\Delta(I_x \mu_x) = \hbar J_x \Delta M_{xx} \tag{3}$$

We shall use the subscript 1 to denote the atom where an isotopic substitution is made and label the molecular axis as the y axis, the positive direction pointing from atoms 1 to 2. If y_1 and y_1' denote the coordinates of atom 1 referred to the center of mass of the molecule before and after isotopic substitution, then it is found that

$$y_1' - y_1 = - \frac{y_1 \Delta M_1}{M_1 + M_2 + \Delta M_1} \tag{4}$$

where M_i denotes the mass of atom i and ΔM_1 is the change in mass of atom 1 upon isotopic substitution. This relation may be used to find ΔI_x. The expression for ΔM_{xx} has been given by Townes et al.[2] Thus (3) becomes

$$I_x \Delta \mu_x + \frac{(M_1+M_2)\,\Delta M_1}{M_1+M_2+\Delta M_1}\, y_1^2\, \mu_x' = \frac{\hbar\, 2 J_x M_p}{|e|} \cdot d \cdot \frac{-y_1 \Delta M_1}{M + M_2 + \Delta M_1} \tag{5}$$

$$- y_1 = \frac{M_2}{M_1+M_2} \cdot r_e \tag{6}$$

where μ_x' is the rotational magnetic moment of the molecule after isotopic substitution, M_p is the proton mass, e the electron charge and r_e the equilibrium bond length. d is the dipole moment (defined positive for $M_1^- - M_2^+$). We shall denote the first term on the left-hand-side of (5) by A and the second term by B.

When the rotational magnetic moment data of Rosenblum et al. for different isotopic species of CO are used in (5), the following results are obtained as shown in Table 1 (atomic masses from Leighton,[6] equilibrium bond length $r_e = 1.12826$ Å from the rotational constants of CO isotopic species reported by Rosenblum et al.[1]).

Thus we see that the four sets of data do not give entirely consistent signs for the dipole moment of CO. It appears that,

Table 1. Determination of the sign of the dipole moment of CO from isotopic variation of rotational magnetic moments

Isotopic substitution	A	B	A+B	Sign of dipole moment
$^{12}C^{16}O \rightarrow {}^{12}C^{18}O$	0.11244913	-0.11212146	0.0003	$C^{+}O^{-}$
$^{12}C^{16}O \rightarrow {}^{13}C^{16}O$	0.10529010	-0.10349639	0.0018	$C^{-}O^{+}$
$^{12}C^{16}O \rightarrow {}^{14}C^{16}O$	0.19608753	-0.19166585	0.0044	$C^{-}O^{+}$
$^{13}C^{16}O \rightarrow {}^{14}C^{16}O$	0.09498496	-0.09235699	0.0026	$C^{-}O^{+}$

regardless of the method of data treatment, this inherent uncertainty of the experimental results would remain. Clearly this arises from the same limitation that is present in ab initio calculations.

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PROPOSITION III The Vibrational Force Constant and the Equilibrium Bond Length of the Hydrogen Molecule

The derivation of a relation between the vibrational force constant and the equilibrium bond length in the hydrogen molecule from Heitler-London theory is proposed.

In 1934, Badger[1] proposed his empirical equation

$$k^{-1/3} = a_{ij}(r_e - b_{ij})$$

relating the vibrational force constant k with the equilibrium bond length r_e through the constants a_{ij} and b_{ij} which have values depending on the nature of the bonded atoms. With this equation, Badger was able to correlate a large amount of spectroscopic data. The equation has also been demonstrated to be of predictive value.[2]

Much effort has been spent in attempting to understand the theoretical basis for the equation[3] but these efforts have not yet been successful. A simple general relationship is evidently very hard to obtain from first principles. We therefore propose that the simplest molecule of all, the hydrogen molecule, be examined prior to any investigation of more general molecular systems.

The hydrogen molecule is unique in that its total electronic energy can be obtained as a function of the internuclear separation in closed form by using the Heitler-London wavefunction. This wavefunction is[4]

$$\psi = \sqrt{\frac{1}{2(1+S^2)}}\,[a(1)\,b(2) + b(1)\,a(2)][\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$$

where a(1) and b(1) are normalized Slater 1s atomic orbitals of electron 1 centered on atom a and b, respectively, and

$$S = \int a(1)\,b(1)\,dv_1$$

The total energy of the molecule corresponding to this wave-function is given by [4]

$$E(R) = \frac{2\alpha^2}{1+S^2}(1 - KS - S^2)$$

$$+ \frac{\alpha}{1+S^2}(-4 + 2J + J' + 4KS + K') + \frac{2\alpha}{w}$$

where R is the internuclear separation, $w = \alpha R$, and α is the orbital exponent. The terms K, S, etc. are given explicitly in Slater [4] and we shall reproduce here only the expression for K′:

$$K' = \frac{2}{5}\{-e^{-2w}(-\frac{25}{8} + \frac{23}{4}w + 3w^2 + \frac{1}{3}w^2)$$

$$+ \frac{6}{w}[S^2(C + \ell n\, w) + S'^2\,Ei(-4w) - 2SS'\,Ei(-2w)]\}$$

where $S' = e^w(1 - w + \frac{1}{3}w^2)$

C = Euler's constant

and $$Ei(-x) = -\int_x^\infty \frac{e^{-t}}{t}\, dt; \qquad x > 0$$

E(R) may be expanded in a Taylor series about the equilibrium internuclear distance $R = R_0$:

$$E(R) = E(R_0) + E'(R_0)(R - R_0) + E''(R_0)\frac{(R - R_0)^2}{2} + \cdots\cdots$$

where $E(R_0) = -D$, the dissociation energy (1)

and $E'(R_0) = 0$ (2)

The force constant is given by

$$k = -E''(R_0) \tag{3}$$

In practice, the Taylor expansion has to be made for each of the terms KS, S^2, etc. A preliminary effort at carrying out these expansions has indicated that a certain amount of bookkeeping would be involved. The expansion for K′ contains $Ei(-4\alpha R_0)$ and $Ei(-2\alpha R_0)$. It would be desirable to express these exponential integrals in terms of more easily identifiable quantities. They can possibly be eliminated using the conditions (1) and (2).

There is no doubt that a relation between the force constant and the equilibrium bond length R_0 can be obtained for the hydrogen molecule using the above procedure. The question appears to be whether

or not the relation has any interesting features and whether it can be reduced to a form comparable to Badger's equation in simplicity.

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PROPOSITION IV The Stability and Structure of Bound Molecular Dimers in Gaseous Hydrogen and Oxygen

A theoretical construct is proposed with the object of elucidating the stability and structure of bound molecular dimers in gaseous hydrogen and oxygen.

Direct spectroscopic evidence for bound states of dimeric hydrogen at low temperatures has been reported by Watanabe and Welsh[1] in 1964. More recently, indirect evidence for bound dimers of oxygen molecules has been reported by Blickensderfer and Ewing,[2] following evidence obtained by Badger and collaborators[3] for the existence of collision pairs of oxygen molecules at room temperature.

The evidence in the case of oxygen consists of a dramatic increase in induced absorption in the (0-0) band of the $(^1\Delta_g - {}^3\Sigma_g^-)$ system as the temperature is lowered to 87°K. The evidence in the case of hydrogen consists of fine structure in the pressure-induced fundamental infrared band components in addition to an increase in the absorption coefficient. The frequencies of the eight absorption maxima observed were successfully expressed in the form

$$\nu = \nu_{H_2} + (\nu_{\ell'} - \nu_{\ell''})$$

where ν_{H_2} is one of the transition frequencies of the free hydrogen molecule, $Q_1(0)$, $S_1(0)$, and $Q_1(0) + S_1(0)$. The ν_ℓ's are a set of four frequencies with $\ell'' = 0, 2$ and $\ell' = 1, 3$. The integer ℓ was identified with the quantum number of the angular momentum of the relative

motion of the two H_2 molecules. From the deduced effective rotational constant of the dimeric molecule, the equilibrium internuclear separation in the dimer was estimated to be in the range 4.2 - 4.6 Å.

Previously, the existence of bound dimeric oxygen molecules has been predicted by Stogryn and Hirschfelder.[4] Approximating the intermolecular potential by a Lennard-Jones potential function and using the WKB energy-level condition for a particle moving in a potential well, they predicted that the maximum number of bound vibrational levels in $(0_2)_2$ is 8 and estimated the dimer concentrations to be very small at several temperatures.

In view of the low concentration of molecular dimers in both hydrogen and oxygen gases, experimental characterization of their stability and structure is difficult. We therefore propose an approximate theoretical construct in order to facilitate experimental investigations. The basic construct is essentially that used by Bernardes and Primakoff[5] in their theoretical investigation of molecule formation in the inert gases. These investigators fitted a Lennard-Jones interatomic potential function to a Morse potential function for which the Schrödinger equation can be solved to give the energy eigenvalues in closed form.

The intermolecular potential function of two identical homonuclear diatomic molecules may be written as[6]

$$V = V^{(dis)} + V^{(Q)} + V^{(val)}$$

where $V^{(dis)}$ is the dispersion energy, $V^{(Q)}$ the electrostatic quadrupole-quadrupole interaction energy, and $V^{(val)}$ the valence energy arising from overlap of the wavefunctions.

An approximate form of the dispersion energy has been obtained by Gray and Van Kranendonk[7] while the form of the quadrupolar energy has been given by Van Kranendonk.[8] If r is the intermolecular distance and θ_i, ϕ_i are the polar angles of the internuclear axis of molecule $i = 1, 2$ relative to the intermolecular axis as polar axis, then

$$
\begin{aligned}
V^{(dis)} = -4\epsilon\left(\frac{\sigma}{r}\right)^6 \Bigg\{ & 1 + 4\pi\left(\frac{4\pi}{5}\right)^{1/2} \frac{(\gamma/\alpha)}{\sqrt{45}} \\
& \cdot \Bigg[\sum_m C(202; m\,0)\, Y_{2,m}(\theta_1, \phi_1)\, Y_{0,0}(\theta_2, \phi_2)\, Y^*_{2,m}(0, 0) \\
& + \sum_m C(022; 0m)\, Y_{0,0}(\theta_1, \phi_1)\, Y_{2,m}(\theta_2, \phi_2)\, Y^*_{2,m}(0, 0) \Bigg] \\
& + 4\pi\left(\frac{4\pi}{9}\right)^{1/2} \frac{(\gamma/\alpha)^2}{45} \frac{36}{\sqrt{70}} \\
& \cdot \sum_{m\, m_2} C(224; m_1 m_2)\, Y_{2,m_1}(\theta_1, \phi_1)\, Y_{2,m_2}(\theta_2, \phi_2) \\
& \qquad Y^*_{4,m_1+m_2}(0, 0) \Bigg\}
\end{aligned}
$$

and

$$
V^{(Q)} = \frac{4\pi Q^2}{r^5} \sum_{m=-2}^{2} a_m\, Y_{2,m}(\theta_1, \phi_1)\, Y^*_{2,m}(\theta_2, \phi_2)
$$

where ϵ and σ are the usual parameters in the Lennard-Jones

intermolecular potential function. γ and α are the anisotropy and the average value of the polarizability of the monomeric molecule and Q the molecular quadrupole moment. $C(\ell_1 \ell_2 \ell;\ m_1 m_2)$ is the Clebsch-Gordan coefficient and $a_2 = a_{-2} = 1$, $a_1 = a_{-1} = -4$, $a_0 = 6$. The spherical harmonics are as defined in Condon and Shortley.[9]

The dependence of the valence energy $V^{(val)}$ on r may be taken to be an inverse twelfth power repulsion as in the usual Lennard-Jones potential function. The dependence on θ_i, ϕ_i (i = 1, 2) will, in general, consist of all possible orders of spherical harmonics allowed by the inversion symmetry of each molecule. However, from the forms already obtained for $V^{(dis)}$ and $V^{(Q)}$, it appears to be a convenient approximation to restrict $V^{(val)}$ to be of the following form:

$$V^{(val)} = 4\left(\frac{\sigma}{r}\right)^{12}\left[1 + \sum_{m=-2}^{2} b_{|m|}\, Y_{2,m}(\theta_1\phi_1)\, Y^{*}_{2,m}(\theta_2, \phi_2)\right]$$

where the $b_{|m|}$'s are constants.

The constants ϵ, σ, and $b_{|m|}$ may be obtained from data for the second virial coefficient B(T) at high temperatures by inversion of the formula

$$B(T) = \frac{N}{4}\int_0^{\infty}\int_0^{2\pi}\int_{-1}^{1}\int_{-1}^{1}(1 - e^{-V/kT})\, d(\cos\theta_1)\, d(\cos\theta_2)\, d(\phi_2 - \phi_1)\, r^2\, dr$$

where N is Avogadro's number. It has, however, been shown that the inversion of second virial coefficient data gives uniquely only the

positive single-valued part of the intermolecular potential as a function of internuclear separation; the potential well cannot be uniquely determined and only its width as a function of its depth can be obtained.[10] It is proposed that this lack of uniqueness be partially resolved through the determination of the long-range part of the potential from thermal-energy molecular-beam scattering data, as has recently been reviewed by Bernstein and Muckerman.[11] The total cross section for H_2 - H_2 scattering has been reported by Minten and Osberghaus[12] who have in fact deduced a value for the orientation-averaged inverse sixth-power van der Waals attraction constant. Similar data for O_2 -O_2 scattering have yet to become available, however. In view of the unique nature of the systems, a detailed investigation of both H_2 - H_2 and O_2 - O_2 thermal-energy scattering is clearly of importance.

The form of the intermolecular potential function $V(r, \theta_1, \phi_1, \theta_2, \phi_2)$ having thus been specified, we propose to study the relative translational motion of two homonuclear diatomic molecules by neglecting the vibrational and rotational degrees of freedom of each molecule. For a fixed set of angles $\theta_i = \theta_i'$, $\phi_i = \phi_i'$, $i = 1, 2$, we have the intermolecular potential as a function of r only. This can now be fitted to the Morse potential

$$V_M(r) = D\left[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right]$$

Ideally, the three parameters D, α, and r_0 should be determined by

requiring $V_M(r)$ to have a second-order contact with $V(r, \theta_1', \phi_1', \theta_2', \phi_2')$ at the position of the latter's minimum. From the form of $V(r, \theta_1', \phi_1', \theta_2', \phi_2')$, however, it would instead appear to be more convenient to require functions and derivatives (up to second order) to match at the point

$$r = 2^{1/6}\sigma$$

where the isotropic Lennard-Jones potential is a minimum.

The energy eigenvalues of the Schrödinger equation for the relative translational motion governed by the potential function $V_M(r)$ have been given in Pauling and Wilson.[13]

If μ is the reduced mass of the collision pair, and if $\hbar^2/(2\mu r_0^2 D) \equiv x^2 \ll 1$, then[5, 13]

$$\frac{E_{K,s}}{D} = -\left[1 - 6x\left(s+\tfrac{1}{2}\right)\right]^2 + x^2 K(K+1)$$

$$- \frac{5}{2} x^3 K(K+1)\left(s+\tfrac{1}{2}\right)$$

$$s = 0, 1, 2 \cdots s_{max}; \quad K = 0, 1, 2 \cdots K_{max}(s)$$

Bound vibrational states of the dimeric molecule are given by negative values of $E_{K,s}$. The maximum number of bound vibrational states is $(s_{max} + 1)$ and occurs for $K = 0$.

It may be that no negative eigenvalues are found, in which case we rule out the assumed set of orientation angles $\theta_i = \theta_i'$, $\phi_i = \phi_i'$,

$i = 1, 2$ in considering the possible structure of the stable dimeric molecule. However, from the spectroscopic evidence cited earlier, we can expect that at least one set of orientation angles would lead to negative eigenvalues.

By requiring each molecule to have only translational freedom, we have neglected the possibility of a change in rotational state accompanying the translational motion. In this respect, our construct is therefore no better than that of Stogryn and Hirschfelder.[4] However, we do allow the intermolecular potential function to be anisotropic. A possible check on the usefulness and results of the construct exists in that the spectroscopic evidence of Watanabe and Welsh[1] indicate the existence of probably two bound states in $(H_2)_2$.

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PROPOSITION V The Position and Height of the Potential Maximum in $He_2(1s^2,\ 1s\,2s;\ {}^3\Sigma_u^+)$

Experimental and theoretical evidence available at the present time[1] shows quite conclusively the existence of a maximum in the interatomic potential function of $He_2(1s^2,\ 1s\,2s;\ {}^3\Sigma_u^+)$. It is proposed that the height and location of this maximum be estimated by establishing the limiting curve of dissociation[2] from spectroscopic data and from the velocity dependence of the total cross section for the scattering of $He^*(1s\,2s,\ {}^3S)$ metastable atoms from ground-state $He(1s^2,\ {}^1S)$ atoms.

If $U_0(r)$ is the interatomic potential function (in units of cm^{-1}) of two atoms, then the effective potential in the equivalent one-body problem is given by

$$U_J(r) = U_0(r) + \frac{1}{hc} \cdot \frac{\hbar^2}{2\mu r^2} J(J+1)$$

where μ is the reduced mass and J the quantum number of rotational angular momentum of the pair of atoms. If $U_0(r)$ has a maximum, say, at $r = r_m$, then Herzberg[3, 2] has very early pointed out that the maximum in $U_J(r)$ will always occur at the same value of r, at least for small values of J. Hence a plot of the maximum energies of $U_J(r)$ against J(J+1) (limiting curve of dissociation) should give a straight line with slope equal to

$$\frac{1}{hc} \cdot \frac{\hbar^2}{2\mu r_m^2}$$

The intercept of the straight line is $U_0(r_m)$. From the slope and intercept, the location and height of the potential maximum may therefore be determined.

Limiting curves of dissociation may be established by plotting rotational term values in each vibrational level as a function of $J(J+1)$. Providing the effect of quantum mechanical tunneling through the potential barrier is negligible, the last observed term value in each vibrational level lies just beneath the potential maximum in $U_J(r)$ while the first missing term value corresponds to a predissociated level that lies just above the maximum. The limiting curve of dissociation must pass through these two points.

A number of rotational term values for each of several vibrational levels in $He_2(1s^2,\ 1s\,2s;\ {}^3\Sigma_u^+)$ may be obtained from the spectroscopic data of Ginter [4] who has recently observed and analyzed the $3p\sigma,\ {}^3\Sigma_g^+ \rightarrow 2s, {}^3\Sigma_u^+$ emission band system of He_2. However, Ginter was apparently unsuccessful in extending the rotational analysis far enough to unambiguously identify the expected predissociation phenomena and therefore the construction of the limiting curve of dissociation from his data alone is not possible at the present time. It is proposed that, in order to complement the spectroscopic data and establish the limiting curve of dissociation, the total cross section for the scattering of metastable $He^*(1s\,2s,\ {}^3S)$ atoms from ground-state

$He(1s^2, {}^1S)$ atoms be obtained as a function of relative velocity.

It is known[5] that as the relative kinetic energy of two atoms is increased, the scattering phase shift η_J corresponding to $U_J(r)$ increases abruptly by π whenever the energy passes through the energy level of a quasi-bound state [semi-discrete state with energy above the energy of dissociated atoms but below the potential maximum of $U_J(r)$]. This increase in the phase shift is manifested as a resonance (a maximum and/or a minimum) in the total scattering cross section Q(v) as a function of the relative velocity v.

Bernstein[5] has pointed out that only for the states of short lifetimes [i.e., the levels near the maximum in $U_J(r)$] will resonance widths in the scattering cross section be sufficiently large to allow observation of the resonances in Q(v) with presently available experimental velocity resolution. He further emphasized that these are just the levels which are too broad for spectroscopic observation. This consideration therefore shows that the location of the resonances in Q(v), together with a plot of spectroscopically observed rotational term values in each of a number of vibrational levels as a function of J(J+1), would determine the limiting curve of dissociation. The same consideration might also possibly provide one reason for the absence of resonances in the velocity dependence of the cross section for scattering of metastable $He^*(1s\,2s, {}^3S)$ atoms from ground-state $He(1s^2, {}^1S)$ atoms as obtained by Rothe et al.[6] Rothe and collaborators obtained the total scattering cross section in the range of relative velocities 1000-3300 meters/sec. However, if the recent ab initio

calculations of Matsen and collaborators [1] are accurate enough, then the height of the maximum in the interatomic potential function is about 0.15 ev. This corresponds to a relative velocity of 3,800 meters/sec. It is therefore proposed that the measurements of Rothe and collaborators be extended to higher relative velocities.

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